# EXAMINATION OF WATER

## FOR SANITARY AND TECHNICAL PURPOSES

LEFFMANN

FIFTH EDITION

# EXAMINATION OF WATER.

LEFFMANN.

BY THE SAME AUTHOR.

---

## Sanitary Relations of the Coal-tar Colors.

BY THEODORE WEYL.

AUTHORIZED TRANSLATION.

12mo. 154 pages. $1.25.

---

## Handbook of Structural Formulae.

ntaining 180 Structural Formulæ (with alternate pages blank).

12mo. $1.00.

---

## Analysis of Milk and Milk Products.

Second Edition, Revised and Enlarged.
12mo. Illustrated. 120 pages. $1.25.

---

## Select Methods in Food Analysis.

BY HENRY LEFFMANN AND WILLIAM BEAM.

8vo. 374 pages. $2.50.

# EXAMINATION OF WATER

FOR

# SANITARY AND TECHNIC PURPOSES.

BY

HENRY LEFFMANN, A.M., M.D., PH.D.,

PROFESSOR OF CHEMISTRY IN THE WOMAN'S MEDICAL COLLEGE OF PENNSYLVANIA AND IN THE WAGNER FREE INSTITUTE OF SCIENCE; PRESIDENT OF THE ENGINEERS' CLUB OF PHILADELPHIA 1901; VICE-PRESIDENT (BRITISH) SOCIETY OF PUBLIC ANALYSTS 1901–02; CHEMIST STATE BOARD OF HEALTH OF PA. (EASTERN DISTRICT.)

*FIFTH EDITION, REVISED AND ENLARGED, WITH ILLUSTRATIONS.*

PHILADELPHIA
P. BLAKISTON'S SON & CO.
1012 WALNUT STREET
1904

I DEDICATE THIS BOOK TO THE

MEMORY OF

**My Mother,**

TO WHOSE WISE PRECEPT AND EXAMPLE

IN MY BABYHOOD

I OWE WHATEVER MERIT MY MANHOOD YEARS

MAY SHOW.

—If thou couldst, doctor, cast
The water of my land.

# PREFACE.

In the present edition, numerous revisions have been made but the plan of the book has not been disturbed. In the four editions which have been issued, it has seen notable changes in the attitude of experts toward certain methods. When the first edition was issued, under the joint authorship of Dr. William Beam and myself, bacteriologists were enthusiastically claiming to be able to determine absolutely the presence or absence of disease-producing microbes in water, and asserting that sanitary analysis of water by chemical methods was about to become a matter of history. At present, the limitations of bacteriology are evident, and the value of routine chemical analysis is generally recognized. Upon this point, and also on the question of the inherent danger of unfiltered surface water even when not receiving sewage directly, the book took decided stand, and the development of the views of experts has fully justified it. Long experience has convinced me that for determining the potability of water, the determinations of chlorin, nitrates and nitrites afford the most satisfactory indications, and that the figures for nitrogen or ammonium (so-called "free ammonia") and nitrogen by permanganate (so-called "albuminoid ammonia") are of much less value than is generally supposed. The suggestion of Woodman, that phosphates afford a useful datum, is worthy of special attention.

*119 South Fourth Street,*
*Philadelphia, November, 1903.*

# CONTENTS.

# NOTE ON WATER-SUPPLY.

The human race must have recognized at an early period the value of an abundant supply of pure and refreshing water. Pastoral communities would be obliged to guide their movements along lines that would keep them within convenient reach of streams and pools for watering cattle; agricultural nations could only establish themselves where water was abundant. Of the two classes, the former would be much less likely to develop soil-pollution, and, accordingly, we find that it is with agricultural and manufacturing centers—*i. e.*, towns and cities—that the serious difficulties with regard to water-supply arise. Drainage areas are easily polluted; in all the civilized countries the streams receive more or less sewage, and are correspondingly offensive to the senses and dangerous to health. The subsoil is better adapted to deal with normal pollution, but its powers are not inexhaustible, and in time wells and springs become unsafe. The usual course of events in this matter is well portrayed by Sextus Julius Frontinus, who was Water Commissioner of Rome from A. D. 97 to 103, and who has left us a comprehensive account of the water-supply of that city. He says that from the building of the city until its four hundred and forty-first year (312 B. C.), the citizens were supplied with water from the Tiber, or from wells and springs. These springs, as with other nations of antiquity, were often credited with healing powers, either due to some medicinal ingredients or because the locality was supposed to be the abode of a minor deity, whose favor could be secured in various ways. The Roman water-supply became unsatisfactory; aqueducts were built, and these supplied the city for centuries. Two of the original aqueducts are still in use, supplying modern Rome with excellent water. The quantity of water supplied to the ancient city during the height of the development of the aqueduct system—the early part of the second century of the Christian era—is not accurately known, but Clemens Herschel, after careful examination of all data, fixes it at about 50,000,000 gallons a day. Most of the supply was of good quality, but some of the aqueducts delivered river water that was frequently turbid. No proper filtering basins were in use, but special interrupting chambers assisted in getting rid of the coarser suspended matters.

Much less is known of the water-supply of the other great cities of the ancient world. Aristotle, in his "Constitution of Athens," refers to an official designated "Superintendent of Springs," which shows that municipal hygiene was not wholly overlooked in that city. Jerusalem, during its influential period, was apparently well supplied with water. The remains of underground conduits have been lately discovered, including a tunnel cut through rock to a point distant about 300 meters in a direct line, but an actual length much greater on account of the tortuous course. This tunnel was probably executed in the reign of Hezekiah (eighth century B. C.). An inscription found on the interior wall some years ago, states that the tunnel was bored from each end and the borers met nearly in line. It leads from a spring, now called the Virgin's Spring (considered as identical with the ancient Gihon), to a point near the Pool of Siloam, at the southeast corner of the city.

In common with the general decline of intelligence and morals which affected Europe during the thousand years from the fifth to the fifteenth century, the protection of the water-supply was but little regarded. The aqueducts of Rome, Athens, and Lyon fell into disuse, and even at present are mostly represented by a few scattered ruins studied only by the antiquary and historian.

It is not appropriate to discuss the engineering features of ancient or modern water-supply, but it is worth while to correct a wide-spread error in regard to the Roman engineers. It is often said that they did not know that water will rise to its original level, and, therefore, built extensive aqueducts to carry water over valleys. The fact is that they were as fully aware of the principle as modern engineers, but it was usually cheaper for them to build the aqueducts than to use inverted siphons. They did use the latter at times. In the first century of the Christian era, an aqueduct for supplying Lyon (Lugdunum) was provided with a series of seven lead pipes, each about 20 centimeters in diameter, to carry water across a deep valley.

# NATURAL HISTORY AND CLASSIFICATION OF WATER.

Pure water is an artificial product. Natural waters always contain foreign matters in solution and suspension, varying from mere traces to very large proportions. The properties, effects, and uses of water are considerably modified by these ingredients, and the object of analysis is to ascertain their character and amount. Since these are largely dependent on the history of the water, a classification based on this will be convenient. We may distinguish four classes of natural waters:

*Rain Water.*—Water precipitated from the atmosphere under any conditions, and therefore including dew, frost, snow, and hail.

*Surface Water.*—All collections of water in free contact with the atmosphere, as in streams, seas, lakes, or ponds.

*Subsoil or Ground Water.*—Water not in free contact with the atmosphere, percolating or flowing through soil or rock at moderate distance below the surface, and derived in large part from the rain or surface water of the district.

*Deep or Artesian Water.*—Water accumulated at considerable depth below the surface, from which the subsoil water of the district has been excluded by difficultly permeable strata.

**Rain water,** when gathered in the open country and in the later period of a prolonged rain or snow, is the purest form of natural water. When collected directly, it contains but little solid matter, this consisting principally of ammonium compounds and particles of organic matter, living and dead, gathered from the atmosphere. In districts near the sea an appreciable amount of chlorids will be present. It is obvious that a prolonged rain will wash out the air, but since storms are usually attended by wind, fresh portions of air are continually flowing in, and thus the water never becomes perfectly pure. Rain water collected in inhabited districts is usually quite impure.

**Surface Water.**—Rain water in part flows off on the surface, and gains in the proportion of suspended and dissolved matters, the former being found in large amount when the rainfall is profuse. The wearing action of water is dependent on the amount and character of these suspended materials. From the higher levels of a watershed, the streams, more or less in the form of torrents, gather into larger currents, and, reaching lower levels, become slower in movement, and deposit much of the suspended matter. By admixture of the waters from widely separated districts the character and amount of the dissolved matters are much modified.

It is obviously impossible to establish close standards of composition for surface waters. In the case of rain water, falling on the surface of undisturbed, unpopulated territory, the amount of solids dissolved will be small, and will consist principally of carbonates and sulfates. The water of lakes and rivers is, however, in part derived from springs, which may proceed from great depths, and thus introduce substances not easily soluble in surface water, nor derivable from the soil of the district.

The exposure to light and air which surface water undergoes, results in the absorption of oxygen and loss of carbonic acid, together with the oxidation of the organic matter. The diminution of the rapidity of the current permits the deposition of the suspended matters, and this occurs especially as the river approaches the sea, not only from the retarding influence of the tidal wave, but from the precipitating action of the salt water.

**Subsoil Water.**—Water that penetrates the soil passes to various depths, according to the porosity and arrangement of the strata. As a rule, it descends until it reaches but slightly pervious formations, upon the level of which it accumulates. In the upper layer of soil it dissolves mineral and organic ingredients, and becomes impregnated with microörganisms, through the agency of which the organic matter undergoes important transformations. The water, constantly accumulating, gradually flows along the incline of the impervious stratum, or through its fissures, and may either pass downward or emerge in the form of a spring.

Much difference is observed in the composition of subsoil waters, but as a general rule they contain small amounts of mineral substances and organic matter. In populated districts, however, a marked change is produced through admixture with water containing animal and vegetable products in various stages of decomposition. It is especially the organic matter containing nitrogen that is of importance. These are mostly unstable, and decompose, partly by oxidation, partly by splitting up into simpler forms; changes in most cases brought about by microörganisms. The nitrogen is in part converted into ammonium compounds, but a considerable portion suffers further oxidation, and in association with the mineral substances present forms nitrites and nitrates, especially the latter. This is called "nitrification."

Nitrification takes place under the influence of microbes, the habitat of which does not extend more than a few yards below the surface of the soil. Several microörganisms with active nitrifying powers have been isolated and described. The nitrifying action is often exerted upon the ammonium compounds formed from the organic matter. The presence of some substance capable of neutralizing acids is usually necessary to continuous action. Calcium and magnesium carbonates fulfil this function. Nitrates are the final result of this action; nitrites are present at any given time only in small quantity. Denitrification—that is, the reduction of nitrates and nitrites to ammonium compounds—takes place also under the influence of microbes, and is especially apt to occur when considerable quantities of decomposing organic matter are introduced. Several species of denitrifying bacilli have been described. A partial reduction sometimes occurs, and a notable proportion of nitrites is found, but in the presence of actively decomposing organic matter, such as that in sewage, a complete reduction, even to the liberation of nitrogen, may occur.

**Deep Water.**—Water which penetrates the fissures of the fundamental rock-formations may pass to great depths, and by following the lines of the lowest and least permeable strata may be transported to points far removed from those at which it was originally collected. The chemical changes thus induced include most of those which take place at higher points, but the increase of pressure and temperature confers increased solvent power. Carbonic acid will accumulate under conditions favorable to the solution of calcium, magnesium, and iron carbonates, and iron, and manganese oxids may be converted into carbonates and then dissolved. Sulfates are reduced to sulfids, and these subsequently, by the action of carbonic acid, yield hydrogen sulfid. Organic matter, living and dead, plays an important part, determining the reduction of ferric compounds to ferrous, and of the sulfates to sulfids, and is itself converted ultimately into ammonium compounds, notable quantities of which are often found in deep waters. Further, it is found that nitrates and nitrites are present only in small amount, except from certain strata rich in organic matter. In some cases the water acquires very high temperature, and dissociation of rocks occurs with solution of considerable amounts of silicic acid, which is ordinarily but sparingly soluble in water.

Masses of water thus accumulated under heat and pressure may find their way to the surface either through natural fissures or be reached by borings.

While no absolute unchangeable line can be drawn between deep and subsoil waters, yet it will in most cases be found that the deep water of a given district, whether obtained through natural or artificial channels, will be decidedly different in composition from the subsoil or surface water of the same, and that the rocks passed through in such cases will be characterized by one or more strata, difficultly permeable to water, and therefore preventing direct communication. The characteristic differences between surface, subsoil, and deep waters are clearly indicated in the table of analyses given in the appendix.

The fact that mere depth is not the essential difference between the two classes of waters is shown by comparison between the composition of the water from a well at Barren Hill, near the northern border of Philadelphia County, and a deep well at Locust Point, Baltimore. The former is a dug well, 130 feet deep; the latter is an artesian boring of 128 feet, which in its descent passes through 4 feet of solid rock. The deeper well is evidently supplied by subsoil water. The artesian well, though located 100 yards from a brackish, sewage-laden estuary, evidently derives no water from it.

| | BARREN HILL WELL. | LOCUST POINT WELL. |
|---|---|---|
| Total solids, | 470.00 | Less than 100.00 |
| Chlorin, | 120.00 | 4.68 |
| Nitrogen as nitrates, | 22.00 | none |

# ANALYTIC OPERATIONS.

## SANITARY EXAMINATIONS.

### COLLECTION AND PRELIMINARY EXAMINATION OF SAMPLES.

Great care must be taken in collecting water samples, in order to secure a fair representation of the supply and to avoid introduction of foreign matters. The five-pint green glass-stoppered bottles used for holding acids are suitable for containing the samples. The contents of one such bottle will suffice for most sanitary or technic examinations. Figure 1 shows a boxed bottle known as "Banker's Glass Can," which I have found very convenient for transportation. It is provided with a hinged lid which can be fastened, if deemed necessary, by a padlock. The green glass-stoppered bottles may be fitted in such an arrange-

FIG. 1.

ment. Crated demijohns are now made for forwarding water. The larger sizes are well adapted for samples which are to be subjected to elaborate analysis. A boxed bottle called the "New Era demijohn" is suitable for water samples. Stone jugs, casks, or metal vessels should not be employed. The bottles used must be thoroughly rinsed several times with the water to be examined, filled, and the stopper tied down or fastened by stretching a rubber finger-cot over the stopper and lip. If corks are used, they should be new and thoroughly rinsed. Wax, putty, plaster, or similar material should not be used.

In taking samples from lakes, slow streams, or reservoirs, it is necessary to submerge the bottle so as to avoid collecting any water that has been in immediate contact with the air. In the examination of public water-supplies, the sample should be drawn from a hydrant in direct connection with the main, and not from a cistern, storage-tank, or dead end of a pipe. In the case of pump-wells, a few gallons of water should be pumped out before taking the sample, in order to remove that which has been standing in the pipe.

In all cases care should be taken to fill the vessel with as little agitation with air as possible.

It is important that with each sample a record be made of those surroundings and conditions which might influence the character of the water, particularly in reference to sources of pollution, such as proximity to cesspools, sewers, or manufacturing establishments. The character and condition of the different strata of the locality should be noted if possible.

Determinations of nitrogen existing as ammonium compounds and as organic matter, and of oxygen-consuming power, should be made upon the sample in the original condition, whether turbid or clear, but all other estimations should be made upon the clear liquid. Turbid waters may be clarified by standing or by filtration; for the latter purpose Schleicher & Schüll's extra heavy No. 598 paper is the best. In many cases the suspended matter can not be entirely removed by filtration, and subsidence must be resorted to. The use of a small quantity of alum, or aluminum hydroxid, as described in the section on the purification of water, will sometimes be applicable as a means of clarifying samples. For the quantitative determination, the sediment from a known volume of the water is collected on a tared filter, dried, and weighed.

Fig. 2.

The water from newly-dug wells is generally turbid, and the determinations are best made after filtration; but the results will be unsatisfactory, showing a higher proportion of organic matter than will be found when the supply becomes clear. For taking samples at considerable depths the bottle shown in Fig. 2 will answer, but samples so collected will not serve for determination of dissolved gases.

**Collection of Samples for Bacteriologic Examination.**—Bacteriologic examinations are of little value unless made promptly on samples that have been collected with precautions against contamination. The inoculation of the culture-medium is best done at the source. If this is not possible, glass-stoppered bottles holding about 200 c.c., which have been thoroughly sterilized, with stoppers in place, in a hot-air oven at 100° C., must be used for collection. They should be rinsed on the *outside* with the water, dipped below the surface, the stopper withdrawn, and again inserted when the bottle is full. If these are to be transported any distance, they should be packed in ice. For the collection of samples below the surface of the water, the bottle shown in the cut (Fig. 2) is recommended by Abbott. The bottle having been previously thoroughly sterilized is sunk to the proper depth and the stopper is then lifted by a special cord and held until the bottle is full, when, the cord being released, the stopper falls. Before taking out portions for test the lip and stopper must be thoroughly sterilized by strong alcohol and by careful heating, and, after cooling, washing with sterilized water.

**Color.**—A colorless glass tube, two feet long and two inches in diameter, is closed at each end with a disc of colorless glass. An opening for filling and emptying the tube should be made at one end, either by cutting a small segment off the glass disc, or cutting out a small segmental section of the tube itself before the disc is cemented on. A good cement for such purposes is the following:

| | | |
|---|---|---|
| Caoutchouc, | 2 | parts. |
| Mastic, | 6 | " |
| Chloroform, | 100 | " |

The ingredients are mixed and allowed to stand for a few days. The cement should be used as soon as solution is effected, as it becomes viscid on standing.

The tube must be about half filled with the water to be examined, brought into a horizontal position, level with the eye, and directed toward a brightly illuminated white surface. The comparison of tint has to be made between the lower half of the tube containing the water under examination and the upper half containing air only.

A more convenient form of tube is made by attaching brass screw-nipples to each end of the tube, and closing these by screw-caps carrying plate-glass discs. Such tubes can be obtained from dealers in chemical apparatus. It is obvious that various methods of comparing color and turbidity may be devised, but data so obtained are of little analytic value, and even that little is limited to samples closely analogous in character.

Hazen has devised a standard for color comparison which he claims as capable of most satisfactory use on all ordinary waters. It is based upon the modification of a solution of platinum chlorid by a solution of cobalt chlorid, as follows:

1.246 grams of potassium platinum chlorid (corresponding to 0.5 gram of Pt) and 1 gram of cobalt chlorid (corresponding to 0.25 gram of Co) are dissolved in water, 100 c.c. of strong hydrochloric acid added, and the solution made up to 1000 c.c. It keeps well, even when exposed to the light. For comparison, 1, 2, 3, etc., of the stock solution are diluted to 50 c.c. in Nessler tubes. These correspond to 0.1, 0.2, 0.3, etc., degrees of the color standard. These also keep for a long time if protected from dust.

Direct comparison in 200 mm. tubes is generally sufficient. If the shade of color is not exactly that of the water, more cobalt may be added, the platinum being constant. Hazen expresses the result in any case in terms of "the amount of platinum in parts per 10,000, which in acid solution with so much cobalt as will match the hue, produces an equal color in distilled water."

Lovibond's tintometer is probably the best means of making color comparisons.

**Odor.**—Put about 150 c.c. of the water into a clean, wide-mouth 250 c.c. stoppered bottle, which has been previously rinsed with the same water; insert the stopper and warm the water in a water-bath to 100° F. Remove the bottle from the water-bath and shake it rapidly for a few seconds; remove the stopper, and immediately note if the water has any smell. Insert the stopper and repeat the test.

In a polluted water the odor will sometimes give a clue to the origin of the pollution.

**Turbidity.**—Several methods for expressing degree of turbidity have been used. Whipple and Jackson, after comparing these, find that finely powdered diatomaceous earth is satisfactory. The material is ignited, ground to a powder that will pass through a 200-mesh sieve, dried at 100° C., cooled in a desiccator, and kept in a well-stoppered bottle. A strong standard is prepared by adding 1 gram of this powder to 1 liter of water, and 12 dilute standards by mixing quantities of the strong standard in amount from 1 to 10 c.c., increasing by 0.5 c.c., to quantities of distilled water sufficient to make 100 c.c. in each case. The dilute standards are kept in tightly corked tubes and shaken several times when used for comparison. If new corks are used, they should well boiled in water to extract coloring-matter. If the sample is of high turbidity, it must be diluted by a known volume of water. The record is made by noting the strength of the standard tube that is nearest in turbidity to the sample, the tubes being held together and viewed from the side. The tube containing the sample must be uniform in size and quality with those containing the standard.

**Reaction.**—The determination of reaction is usually made by the addition of a neutral solution of litmus to the water. If an acid reaction is obtained, the water should be boiled in order to determine if it is due to carbonic acid. Some of the more delicate indicators, such as phenolphthaleïn, lakmoid, and erythrosin, may be used with advantage for these tests. The latter possesses the advantage that it is unaffected by carbonic acid, but detects even traces of free mineral acid. It is neutral, also, to many normal metallic salts, such as ferrous sulfate, which are acid to litmus. Ferric salts, however, are acid to lakmoid. Its color-changes are the same as those of litmus—*i. e.*, red with acids and blue with alkalies.

Phenolphthaleïn is usually applied to the detection of weak acids, such as carbonic acid and the organic acids. In acid and neutral solutions it is colorless; in alkaline, red. Nearly all waters contain carbonic acid, and will therefore bleach a solution of phenolphthaleïn which has been reddened by a small amount of alkali.

## TOTAL SOLIDS.

A platinum basin holding 100 c.c. will be found convenient for this determination. This will weigh about 45 grams. It should be kept clean and smooth by frequent burnishing with sand, a little of which should be placed in the palm of the hand, moistened, and the dish gently rubbed against it. Very fine sea-sand with round, smooth grains is the only kind suitable for this purpose. Coarse river sand, tripoli, or other rough scouring-powders must not be employed. If proper care is taken, the luster of the metal will be retained, and the loss in weight will be trifling. The inner surface can generally be cleaned by treatment with hydrochloric acid, rinsing, and, if necessary, burnishing with sand. Neglect of these precautions will soon lead to serious damage to the dish. A small, smooth slab of iron or marble is convenient to set it on while cooling. When being heated over the naked flame, the dish should rest on a triangle of iron wire, covered with pipe-stems. Dishes of pure nickel are not satisfactory substitutes for those of platinum.

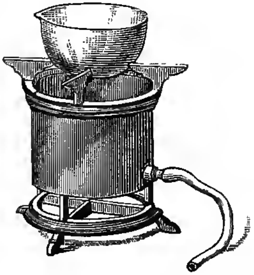


FIG. 3.

Platinum-pointed forceps should be used in handling the dish. The platinum terminals may be kept bright and clean by the use of sand.

The low-temperature burner, used as shown in figure 3, will be found a very convenient substitute for the water-bath and hot-air oven. The inlet pipe is very short and soon becomes so hot as to injure the rubber tube. To avoid this it may be lengthened by means of a piece of ⅛-inch gas-pipe, or the junction may be wrapped with a rag, the ends of which dip into water. By capillary attraction the rag is kept moist and cool.

The determination of total solids is made by evaporating 100 c.c. of the water in the platinum basin, which has been previously heated almost to redness, allowed to cool for ten minutes, and weighed. The operation is conducted at a moderate heat. When the residue appears dry, the heat may be increased slightly for some minutes. The above method will answer in most cases. In waters of exceptional purity it may be advisable to use larger quantities, such as 250 c.c. When the residue contains deliquescent bodies, the determination will not be accurate, and when appreciable amounts of magnesium and chlorin are present, a decomposition will occur toward the close of the evaporation by which magnesium oxid will be formed and hydrogen chlorid escape.

The irregular decomposition occurring during the evaporation may be largely prevented by adding 0.005 gram of sodium carbonate to each 100 c.c. of the sample taken. This converts magnesium and calcium salts into carbonates. The sodium carbonate is conveniently kept in the form of solution of such strength that 1 c.c. contains 0.001 gram. The weight of the carbonate is, of course, to be deducted from the weight of the residue. Drown and Hazen have carefully investigated this method and have found it available for a more satisfactory determination of the loss on ignition. For this process they place the platinum basin containing the residue within another similar basin of such size that an air-space of about one-half of an inch is left all around the inner dish, which is supported upon a spiral of platinum that rests on the bottom of the outer dish. Over the inner dish is suspended a disc of platinum foil to reflect the heat. The outer dish is heated to bright redness.

After the weight of the residue is obtained, the dish should be cautiously heated to low redness and the effect noted. Nitrates and nitrites, calcium and magnesium carbonates, are decomposed; ammonium salts are driven off; potassium and sodium chlorids are also driven off if the temperature is high. Organic matter is at first charred, and by continued heating burned off. When the quantity of nitrates is considerable, slight deflagration may be observed, or the production of red fumes of nitrogen dioxid. The organic matter, in decomposing, not infrequently develops odors which indicate its character or source. These are more satisfactorily observed when a rather large quantity, say 250 c.c., is evaporated at a low heat, preferably on a water-bath.

In water of high organic purity, the residue on heating will give no appreciable blackening nor odor, while in forest streams charged with vegetable matter derived from falling leaves, very decided blackening without unpleasant odor will be noticed. The loss of weight after heating can not be taken as a measure of the organic matter, except when present in relatively large amount.

## CHLORIN.

**Solutions Required:**

*Standard Silver Nitrate.*—Dissolve about five grams of pure recrystallized silver nitrate in distilled water, and make the solution up to 1000 c.c. The amount of chlorin to which this is equivalent may be determined as follows: Several grams of pure sodium chlorid are finely powdered and heated over a Bunsen burner for five minutes, not quite to redness. When cold, 0.824 gram are dissolved in water and the solution made up to 500 c.c. Twenty-five c.c. of this should be treated as below, and the amount of silver solution required noted. Each c.c. of the sodium chlorid solution is equivalent to 0.001 gram chlorin.

*Potassium Chromate.*—Five grams of potassium chromate are dissolved in 100 c.c. of distilled water. A solution of silver nitrate is added until a permanent red precipitate is produced, which is separated by filtration.

**Analytic Process:**

If a preliminary test shows the chlorin to be present in considerable amount, the determination may be made on 100 c.c. of the water without concentration. If, however, there is but little present, 250 c.c. should be evaporated to about one-fifth, best with the addition of a little sodium carbonate, and the determination made on the concentrated liquid after cooling.

The water is placed in a porcelain dish or in a beaker standing on a white surface, a few drops of potassium chromate solution added, and standard silver nitrate solution run in from a buret until a faint red color of silver chromate remains permanent on stirring. The proportion of chlorin is then calculated from the number of c.c. of silver solution added. Greater accuracy is secured by operating in yellow light. A second determination may be made, using as a comparison the liquid first titrated, the red color having been previously discharged by a few drops of sodium chlorid solution.

The water should always be as nearly neutral as possible before titration. If acid, it may be neutralized by the addition of sodium carbonate.

The residue obtained by evaporating the water with sodium carbonate, as described in connection with the determination of the total solids, will often serve conveniently for estimating the chlorin. It is best to use 200 c.c. of the sample and redissolve the residue in about 50 c.c. of distilled water, rubbing the sides of the dish well with a rubber-tipped rod, and then titrating as indicated above.

Chlorin may be determined by Volhard's method, adding excess of standard silver solution, and then titrating the residual silver by means of thiocyanate solution. Free nitric acid does not interfere with this method, but it is necessary to remove the silver chlorid before titrating with thiocyanate. The following description of the method is adapted from Sutton's "Volumetric Analysis":

**Solutions Required:**

*Decinormal Thiocyanate.*—About 10 grams of the potassium compound or 8 grams of the ammonium compound are dissolved in a liter of water and the solution adjusted by means of standard silver nitrate solution.

*Decinormal Silver Nitrate.*—This may be prepared by dissolving pure silver in nitric acid, since as noted above a slight excess of the acid does not interfere with the test.

*Ferric Indicator.*—A saturated solution of ammonium ferric sulfate.

*Nitric Acid.*—This must be free from the lower oxids of nitrogen. They may be removed by adding about one-fourth volume of water and boiling until colorless. The acid should be kept from the light.

**Analytic Method:**

A suitable quantity of the water is treated with a slight excess of decinormal silver nitrate, the chlorid collected by shaking, and an aliquot part of the liquid removed by decantation or filtration. To this is added 10 c.c. of the nitric acid and 5 c.c. of the ferric indicator, and thiocyanate is run in until a faint permanent brown is produced in the liquid. This marks the precipitation of all the silver, and the formation of ferric thiocyanate. The color is seen best by holding the flask against a background of white paper. As the point of precipitation of the last portions of silver is approached, the precipitate becomes flocculent and settles easily. The excess of silver is deducted from the total used; the remainder is the amount required for the chlorin in the water.

## NITROGEN IN AMMONIUM COMPOUNDS AND IN ORGANIC MATTER.

**Apparatus Required:**

*Distilling Apparatus.*—That shown in figure 4 has been found to be convenient. The still consists of a glass retort of about 1000 c.c. capacity. The beak of the retort should incline slightly upward, to prevent contamination by splashing. At about seven centimeters from the end it should be bent at a right angle, and drawn out so as to enter the condensing worm for such a distance as to terminate beneath the level of the water.

The condenser shown in the figure is a copper tank, 33 cm. high, 15 cm. wide, and of length proportioned to the number of distilling vessels operated. The condensing tube is shown only as emerging from the bottom of the tank.

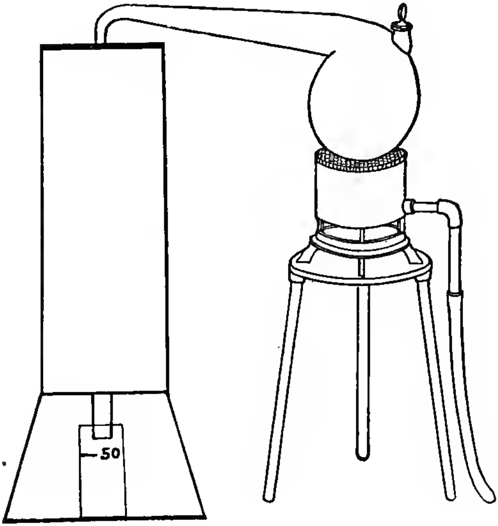


FIG. 4.

Glass worms are apt to break, and it is more satisfactory to use block tin. A piece of rubber tubing is drawn over the junction between the retort neck and worm. A rapid current of cold water should be maintained through the condenser. The heat is applied by means of the low-temperature burner, the iron ring of which is removed so that the retort rests directly on the gauze.

To prevent overheating of the upper part of the retort, a sheet of thick asbestos board about 20 cm. in diameter, with a central opening about 5 cm. in diameter, may be placed on the gauze. With this arrangement the heat is under control, and the danger of breaking the retort is slight. It is advisable to protect the retort from drafts of cold air, which may be done with a cone made of thin sheet asbestos.

Figure 5 shows the distilling arrangement used in the laboratory of the testing station of the Philadelphia filtration plant. The cut was loaned by the *Journal of the American Chemical Society*, and the description is transcribed from the paper published in that journal by G. E. Thomas and C. A. Hall. The flask has a side-neck and ground-glass stopper, and bulb of a capacity of nearly 2000 c.c. It is supported on wire gauze resting on a sheet-iron cylinder. The condensing worm is of block tin connected to the side-neck by rubber tubing, the glass extending into the tin for several centimeters beyond the point of contact of the rubber. Another piece of rubber tubing covers the point of contact of the first piece with the metal tube. The latter is about 9 mm. internal diameter, about 12 mm. external, and is coiled into a helix 6 cm. internal diameter and 11 cm. pitch. The caliber of the tube is expanded slightly at the upper end to allow of insertion of the side-neck of the flask and is contracted for a few centimeters at the outlet. The condenser is made of cold rolled sheet-copper (commercially known as 24 ounce), braced within and provided with a lid hinged at the back and overlapping slightly in front. The water is supplied below and overflows at the top. The ground stoppers and side-neck attachment permit of introduction of samples and solutions without disconnecting the flasks. A long-necked funnel will be convenient for this purpose.

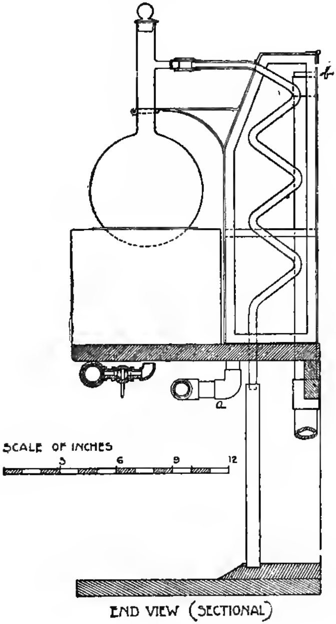


FIG. 5.

Figure 6 shows an elaborate distilling apparatus arranged by R. S. Weston. It has the advantage that the distillate is received on the side on which the distilling

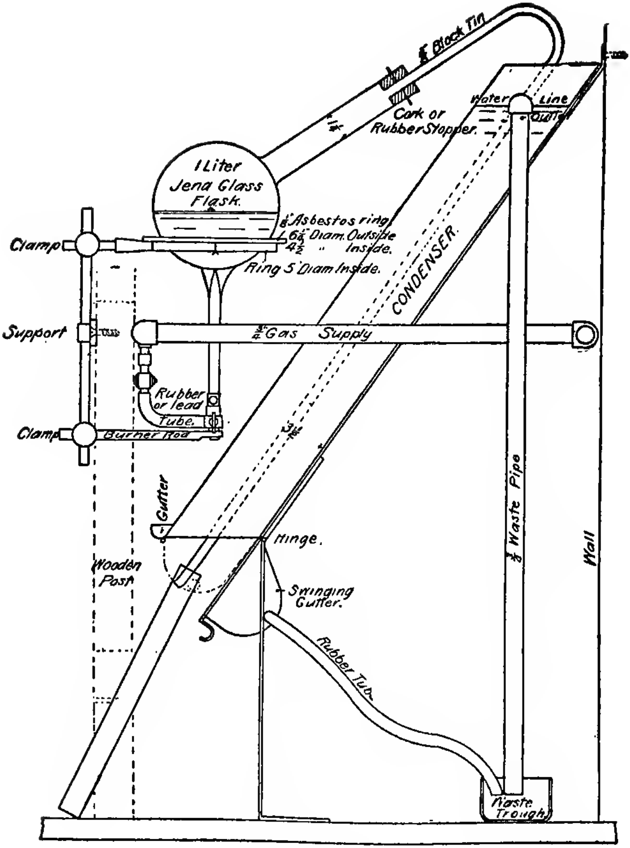
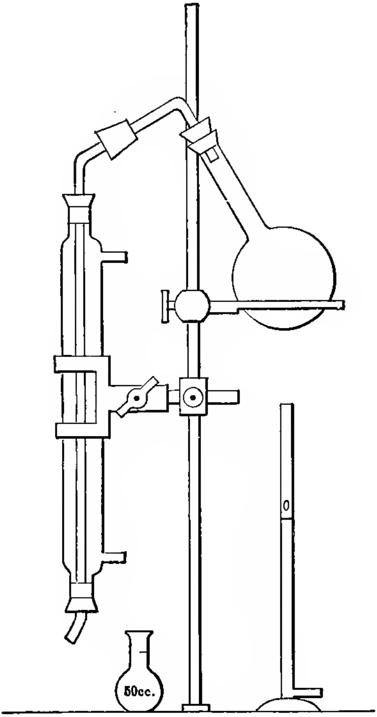

5/8" Block Tin
Cork or
Rubber Stopper.
1¼"
Water Line
Outlet
1 Liter
Jena Glass
Flask.
1/8" Asbestos ring
6¼" Diam. Outside
4½" " Inside.
Ring 5" Diam Inside.
CONDENSER.
Clamp
Support
Clamp
¾" Gas Supply
Rubber
or lead
Tube.
Burner Rod
3½"
Gutter
Hinge.
Wooden
Post
Swinging
Gutter.
Rubber Tube
¾ Waste Pipe
Wall
Waste
Trough

FIG. 6.

flask is placed. The details of construction are indicated in the figure. The condenser may be made of copper or japanned, galvanized iron.



Scale 1½ in.=1 foot.

FIG. 7.

Another convenient form of apparatus is shown in figure 7. It is employed in the laboratory of the Massachusetts

State Board of Health. The joint between the flask and condenser is made by means of a sound cork, into which the condensing tube fits closely; the tube from the flask is made slightly smaller than the condensing tube, and passes into it for about four centimeters.

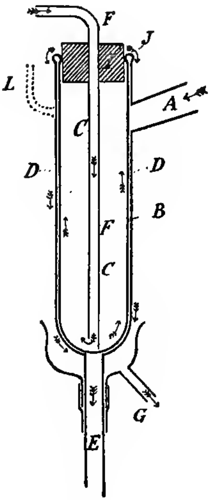


FIG. 8.

A form of condenser applicable to distillations of this character has been devised by Cribb and is shown in figure 8. The vapor passes to a narrow annulus by the tube *A*; the cooling water enters the central portion and overflows, running down the outside wall, being collected by the projecting rim and carried off by the tube *G*. For water analysis a retort with the neck bent at an obtuse angle may be used, or a flask with side tube. In the latter case, the tube must leave the flask at a slight angle upward, and about midway be bent at a slight obtuse angle downward. This prevents contamination of the distillate by spurting. The drawing shows the form given by Cribb, but experience has shown that more space should be allowed between the inner and outer wall at the lowest point, and that the catch-basin should be large. The tube, *G*, should be at least three times the caliber of *F*. It will often be advantageous to wrap a piece of muslin around the body of the apparatus.

*Cylinders for Comparison-color Tests*, about 2.5 centimeters in diameter and holding 100 c.c., made of colorless glass.

**Solutions Required:**

*Sodium Carbonate.*—Fifty grams of pure sodium carbonate are strongly heated, dissolved in 250 c.c. of distilled water, and the solution boiled down to 200 c.c.

*Ammonium-free Water.*—If the distilled water of the laboratory gives a reaction with Nessler reagent, it should be treated with sodium carbonate, about one grain to the liter, and boiled until about one-fourth has been evaporated. Ammonium-free water may be obtained by distilling, in a retort, water made slightly acid with sulfuric acid.

Messrs. J. B. Weems, C. E. Gray, and E. C. Myers recommend the following method: Sodium dioxid is added to ordinary water in the proportion of one gram to a liter, and the liquid boiled for thirty minutes, or longer if the amount of ammonium compounds is high. It is then cooled and the flask kept closed. Flasks holding several liters are most convenient. If the water be distilled, the distillate may also be used for the preparation of standard nitrate and nitrite solutions.

*Standard Ammonium Chlorid.*—Dissolve 0.382 gram of pure dry ammonium chlorid in 100 c.c. of ammonium-free water. For use, dilute 1 c.c. of this solution with pure water to 100 c.c. One c.c. of this dilute solution contains 0.00001 gram of nitrogen.

*Nessler Reagent.*—Dissolve 35 grams of potassium iodid in 100 c.c. of water. Dissolve 17 parts of mercuric chlorid in 300 c.c. of water. The liquids may be heated to aid solution, but must be cooled before use. Add the mercuric chlorid solution to that of the potassium iodid, until a permanent precipitate is produced. Then dilute with a 20 per cent. solution of sodium hydroxid to 1000 c.c., add mercuric chlorid solution until a permanent precipitate again forms; and allow to stand until clear. Nessler and other reagents are best kept in glass-capped bottles, figure 9, in which the pipet may remain when not in use. The solution improves by keeping.

FIG. 9.

*Alkaline Potassium Permanganate.*—Dissolve 200 grams of potassium hydroxid, in sticks, and 8 grams of potassium permanganate, in a liter of distilled water.

The solution may be boiled until about one-fourth is evaporated, and then made up to a liter with ammonium-free water. It will still furnish some ammonium. Fox recommends to distil 50 c.c. with 500 c.c. of absolutely ammonium-free water, best twice distilled with sulfuric acid, and note the ammonia obtained. This quantity should be deducted in each analysis. The method of determining nitrogen by permanganate, as given below, avoids the necessity for this preliminary valuation of the solution.

**Analytic Process:**

The retort and condenser are thoroughly rinsed with ammonium-free water, 500 c.c. of the water to be tested introduced, about five c.c. of the sodium carbonate solution added to render the water alkaline, and some small pieces of pumice-stone or fragments of pipe-stems heated to redness and dropped in while hot. The water is then boiled gently until the distillate measures 50 c.c. The distillate is transferred to one of the color-comparison cylinders, and two c.c. of Nessler reagent added. A yellowish-brown color is produced, the intensity of which is proportional to the amount of ammonium present. The full color is developed in five minutes. This color is exactly matched by introducing into another cylinder 50 c.c. of ammonium-free water, some of the standard ammonium chlorid solution, and two c.c. Nessler reagent, as before. According as the color so produced is deeper or lighter than that obtained from the water, other comparison liquids are prepared containing smaller or larger proportions of the ammonium chlorid, until the proper color is produced.

The distillation is continued, successive portions of 50 c.c. each collected, and tested until no reaction occurs with Nessler reagent. The sum of the figures from the several distillates gives the total nitrogen obtainable as "free ammonia," so called.

If the quantity of ammonium is sufficient to cause a precipitate, the color comparison can not be accurately made. In most cases this will not be of serious moment, as the quantity will be beyond the allowable limit. If accurate determination be desired, it may be made by dividing the first distillate into two equal parts, nesslerizing one of these, and then, if necessary, diluting the second part with ammonium-free water and nesslerizing this.

Occasionally, the evolution of ammonium hydroxid continues indefinitely, and may even increase with successive distillates. This is due, not to ammonium compounds existing as such, but to decomposition of certain nitrogenous bodies, especially urea. In this case it is not advisable to prolong distillation beyond the fourth or fifth distillate, but to proceed to the following part of the process.

The residue in the retort serves for the determination of the nitrogen which is convertible into ammonium by alkaline potassium permanganate—the so-called "albuminoid ammonia" of Messrs. Wanklyn, Chapman, and Smith.

Fifty c.c. of alkaline permanganate solution are added to the retort, the distillation resumed, and the nitrogen estimated in each 50 c.c. as before, deducting that yielded by the permanganate.

It is a practice of some analysts to mix the distillates of each of the foregoing operations, and make determinations merely of the total nitrogen in each case. By so doing, valuable information may be lost, since it has been pointed out by several observers, notably Mallet and Smart, that important information may be gained by observing the rate of evolution of the ammonium hydroxid. Mallet has further pointed out that many waters may contain substitution ammoniums which may pass over before the addition of the alkaline permanganate, but not be correctly measured by nesslerizing. To avoid this error, he suggested that two determinations be made on each sample, one as above described, and the other by the addition of alkaline permanganate without previous distillation. A higher figure may be obtained than the total from the two distillations by the other process.

Since small quantities of ammonium compounds and nitrogenous matters are everywhere present, the greatest care should be exercised in order to avoid their introduction in any way during the course of the analysis. All measuring vessels, cylinders, etc., should be thoroughly rinsed before using. The temperatures of the distillates and standards should be approximately the same when the colors are compared.

The Chemical Section of the American Association for the Advancement of Science recommended the following method for the application of the process:

200 c.c. of distilled water, together with 10 c.c. of the sodium carbonate solution, are distilled down to about 100 c.c. in the retort in which the analysis is to be conducted, and the last portion of 50 c.c. nesslerized to assure freedom from ammonium. Then 500 c.c. of the water to be examined are added, and the distillation is carried on at such a rate that about 50 c.c. are collected in each succeeding ten minutes, and until a 50 c.c. measure of distillate is obtained containing only an inappreciable quantity of ammonia. In nesslerizing, five minutes are to be allowed for the full development of color; after this, no change takes place for many hours.

The distilling vessel is emptied and rinsed thoroughly, 200 c.c. of distilled water and 50 c.c. of alkaline permanganate solution put in, and the liquid distilled down to about 100 c.c., the last portions of the distillate being tested to ascertain freedom from ammonium compounds, another portion of 500 c.c. of the water to be tested is added, and the distillation made as before. The difference between the "free" ammonia of the first operation and the total ammonia of the second is to be taken as the "albuminoid" ammonia.

It is convenient to operate the distilling flasks in pairs, using one of each pair for the permanganate process. Delay and trouble of rinsing are thus avoided. Before beginning an analysis, the greater part of the residue from a previous operation may be drawn off with a siphon, 200 c.c. of distilled water added to each, and the liquids distilled until the reagent shows freedom from ammonium compounds. Suitable portions of the sample are then put in each flask.

For nesslerizing and other color comparisons, many forms of apparatus have been proposed. One, devised by Hehner, is shown in figure 10. It consists of a graduated cylinder with a stop-cock near the base, by which the liquid can be drawn down at will. Two such cylinders may be used—one for the nesslerized distillate, the other for the comparison liquid. The darker liquid is drawn out until the tints are equal, when the relative volumes remaining will give the data for calculation.

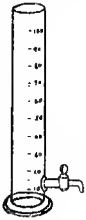


FIG. 10.

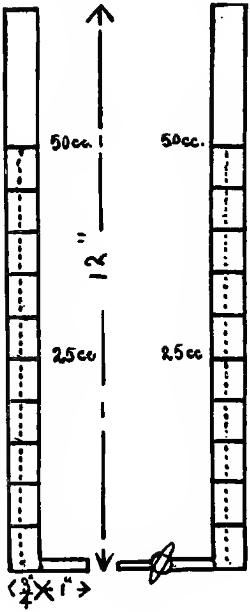


FIG. 11 a.

H. J. Watson has modified the Hehner tube as shown in figure 11. The cuts were loaned by the *Amer. Jour.*

*of Pharmacy.* The jar is 30 cm. long, 1.8 cm. in diameter, and is graduated into cubic centimeters for about 20 cm. from the base. At the side of the base a small tube pro-

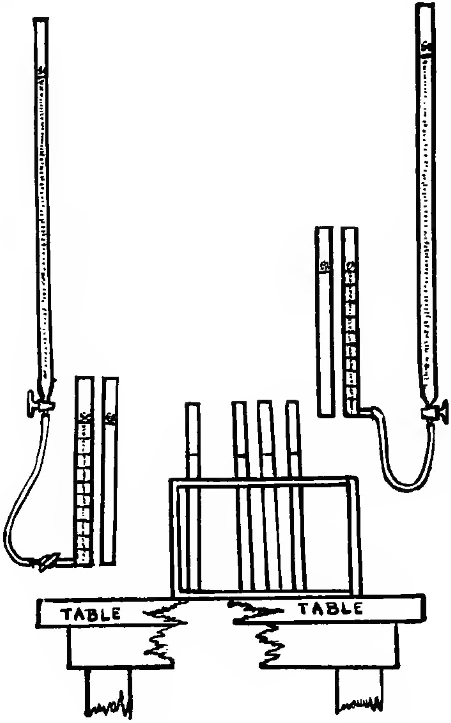


FIG. 11 b.

jects, which may be provided with a stop-cock but it will be seen from one of the figures that this is not necessary.

A number of tubes similar in size and quality of glass to the graduated tube, but marked only at 50 c.c., should be provided. The distillates from the water are placed in the ungraduated tubes, and compared with the tints of the standard ammonium solution, by making the volume of the latter in the graduated tube increase or decrease by means of the stop-cock on the burette and changing the height of the latter.

## TOTAL ORGANIC NITROGEN.

Several processes for the determination of the organic nitrogen in water, based on those in use in ordinary organic analysis, have been devised. That of Frankland and Armstrong requires complex and extensive apparatus and special skill, has been shown also to be liable to inaccuracies, and has not come into extended use.

The ease and certainty with which the nitrogen of most organic bodies may be converted into ammonium sulfate by boiling with sulfuric acid, offers a means of determination free from the objections of former methods. The method introduced by Kjeldahl for general organic analysis was first successfully applied to water analysis by Drown and Martin.

In their original process, 500 c.c. was concentrated to about 300 c.c., and the distillate nesslerized for determining the nitrogen existing as ammonium compounds. The organic nitrogen is then determined in the residual water. Owing to the fact that organic matter may be decomposed by moderate heat, there is liability to underestimation of the nitrogen. It is best, therefore, to determine at once the total unoxidized nitrogen, and estimate, without distillation, on a separate portion of the sample, the nitrogen that exists in ammonium compounds. The procedure is as follows:

**Reagents Required:**

*Concentrated Sulfuric Acid.*—This should be as free as possible from nitrogen. It can now be obtained of high purity.

*Sodium Hydroxid Solution.*—The white granulated caustic soda sold for household use will answer; 350 grams are dissolved in water and made up to 1000 c.c.

*Sodium Carbonate and Hydroxid Solution.*—Twenty-five grams of each are dissolved in 250 c.c. of distilled water, and the solution boiled down to 200 c.c. to free it from ammonium.

**Analytic Process:**

*Determination of Nitrogen Existing as Ammonium.*—Two hundred c.c. of the water are placed in a stoppered bottle, two c.c. each of the solutions of sodium carbonate and sodium hydroxid added, the stopper inserted, the solutions mixed, and allowed to stand for an hour or two. A filter is prepared by inserting a rather large plug of absorbent cotton in a funnel. This should be washed with ammonium-free water until the filtrate gives no color with Nessler reagent. The clear portion of the sample is drawn off with a pipet and run through the filter, the first portions being rejected, since it is diluted by the water retained in the cotton. The filtration is rapid, and when 100 c.c. of the liquid have passed through it, is nesslerized. If but little ammonium is present, a narrow tube about 60 centimeters long should be used for observing the color.

*Estimation of the Total Organic and Ammoniacal Nitrogen.*—Five hundred c.c. of the water are placed in a round-bottomed Bohemian glass flask, ten c.c. of concentrated sulfuric acid added, and a piece of pumice-stone is heated to bright redness and dropped in while hot. The liquid is boiled for an hour after it is colorless, or, at least, quite pale yellow. The flask is allowed to cool, and about 250 c.c. of ammonium-free water added. Fifty c.c. of the sodium hydroxid solution should be placed in the distilling apparatus, about 250 c.c. of water added, a piece of red-hot pumice-stone dropped in, and the liquid distilled until the distillate is free from ammonium. It is best to distil until the retort contains not more than 100 c.c. The sulfuric acid solution is then poured in slowly by means of a funnel, the stem of which touches the side of the retort, so that the two liquids do not mingle. The stopper of the retort is inserted, the liquids mixed by gentle agitation, and distilled. If much ammonium is present, it is advisable to distil the first portion into about ten c.c. of very dilute (1: 1000) sulfuric acid, a piece of glass tube being connected to the condensing worm so that the lower end dips below the surface of the liquid. The distillates are collected and nesslerized in the usual way.

A blank experiment should be made to determine the amount of ammonium in the sulfuric acid.

## NITROGEN AS NITRATES.

**Solutions Required:**

A. H. Gill has subjected the various indirect methods of estimating nitrates to comparative examination, and finds the following method satisfactory:

*Phenoldisulfonic Acid.*—Strong sulfuric acid and pure phenol are mixed in the proportion of 37 grams of the former to 3 grams of the latter, and heated for six hours *in, not upon,* the water-bath. The resulting compound usually solidifies to a white mass on standing, but can be easily liquefied on the water-bath during the evaporation of the samples to be tested.

*Standard Potassium Nitrate.*—0.722 gram of potassium nitrate, previously heated to a temperature just sufficient to fuse it, are dissolved in water, and the solution made up to 1000 c.c. One c.c. of this solution will contain 0.0001 gram of nitrogen.

**Analytic Process:**

A measured volume of the water is evaporated just to dryness in a porcelain basin about six centimeters in diameter. One c.c. of the phenoldisulfonic acid is added and thoroughly mixed with the residue by means of a glass rod. The liquid is then diluted with about 25 c.c. of water, ammonium hydroxid added in excess, and the solution made up to 50 c.c.

The nitrate converts the phenoldisulfonic acid into picric acid, which, by the action of the ammonium hydroxid, forms ammonium picrate; this imparts to the solution a yellow color, the intensity of which is proportional to the amount present.

One c.c. of the standard solution of potassium nitrate is now similarly evaporated in a platinum basin, treated as above, and made up to 50 c.c. The color produced is compared to that given by the water, and one or the other of the solutions is diluted until the tints of the two agree.

The comparative volumes of the liquids furnish the necessary data for determining the amount of nitrate.

The results obtained by this method are satisfactory. Care should be taken that the same quantities of phenoldisulfonic acid are used for the water and for the comparison liquid.

With subsoil and other waters probably containing much nitrates, 10 c.c. will be sufficient; but with river and spring waters, 25 c.c. may be used. When the organic matter is sufficient to color the residue, it will be well to purify the water by addition of aluminum hydroxid and filtration, before evaporating.

Chlorin interferes with the accuracy of the test, but Gill finds that when not amounting to more than 20 parts per million it does not impair the practical value of the results. When greater than this, it is best to evaporate in vacuo over sulfuric acid. If the chlorin be more than 70 parts per million, it should be considerably reduced by the addition of silver sulfate which has been ascertained to be free from nitrates. Nitrites do not influence the reaction.

The following is the process for determining nitrogen as nitrates (and nitrites) recommended by the Chemical Section of the A. A. A. S. It depends upon conversion into ammonium by the copper-zinc couple, and subsequent nesslerizing. It is inferior to the phenoldisulfonic acid method, both in convenience and accuracy, and does not exclude the influence of nitrites.

Take two wide-mouth glass-stoppered bottles, each holding 250 c.c., and a piece of sheet zinc as long and about as wide as the bottles are deep from the shoulder down; clean the zinc by dipping in dilute acid and washing with water, and make it into a loose coil by rolling it around a piece of glass tube. Immerse it in a 1.4 to 1.8 per cent. solution of copper sulfate in ammonium-free water, and leave it there until its surface is well covered with a continuous layer of the black copper; lift it out carefully, cover it in a beaker with successive portions of ammonium-free water, lifting it out and draining each time, and at once put it into one of the bottles of acidified water, prepared as follows:

Make 500 c.c. of the water to be examined distinctly acid with oxalic acid added in fine powder, with constant stirring, so that it shall dissolve readily, and pour half of the liquid into one of these 250 c.c. bottles, and half into the other, and leave them, stoppered, in a warm place for twenty-four hours. Then nesslerize both samples, decanting off the portions, as wanted, from the precipitated earthy oxalates, and using double the usual quantity of Nessler's solution, since the free oxalic acid must be neutralized first by the alkali of the reagent. The proportion of ammonia may often be so large in the water in which the reduction is made, by the copper-zinc couple, that only five or ten c.c. can be taken for each test, and made up to 50 c.c. by the addition of ammonium-free water. The difference between the results with the two portions of water gives the amount of nitrogen due to the oxidized nitrogen compounds in the water examined.

## NITROGEN AS NITRITES.

The following is Ilosvay's modification of Griess's test. It has the advantage over the original method, that the color is developed more rapidly, and the solutions are less liable to change.

**Solutions Required:**

1-4-*amidobenzenesulfonic Acid Solution* (*Sulfanilic Acid*).—Dissolve 0.5 gram in 150 c.c. of diluted acetic acid, sp. gr. 1.04.

*α-amidonaphthalene Acetate Solution.*—Boil 0.1 gram of solid α-amidonaphthalene (α-naphthylamin) in 20 c.c. of water, filter the solution through a plug of washed absorbent cotton, and mix the filtrate with 180 c.c. of diluted acetic acid. All water used must be free from nitrites, and all vessels must be rinsed out with such water before tests are applied, since appreciable quantities of nitrites may be taken up from the air.

*Standard Sodium Nitrite.*—0.275 gram pure silver nitrite is dissolved in pure water, and a dilute solution of pure sodium chlorid added until the precipitate ceases to form. It is then diluted with pure water to 250 c.c., and allowed to stand until clear. For use 10 c.c. of this solution are diluted to 100 c.c. It is to be kept in the dark. One c.c. of the dilute solution is equivalent to 0.00001 gram nitrogen.

The silver nitrite is prepared thus: A hot concentrated solution of silver nitrate is added to a concentrated solution of the purest sodium or potassium nitrite available, filtered while hot, and allowed to cool. The silver nitrite will separate in fine, needle-like crystals, which are freed from the mother liquor by filtration by the aid of a filter pump. The crystals are dissolved in the smallest possible quantity of hot water, allowed to cool, and again separated by means of the pump. They are then thoroughly dried in the water-bath, and preserved in a tightly stoppered bottle away from the light. The purity may be tested by heating a weighed quantity to redness in a tared porcelain crucible and noting the weight of the metallic silver. One hundred and fifty-four parts should leave a residue of 108 parts silver.

**Analytic Process:**

Twenty-five c.c. of the water are placed in one of the color-comparison cylinders, and two c.c. each of the test solutions are dropped in. It is convenient to have a pipet for each solution, and to use it for no other purpose.

One c.c. of the standard nitrite solution is placed in another clean cylinder, made up with nitrite-free water to 25 c.c. and treated with the reagents as above.

In the presence of nitrites a pink color is produced. At the end of five minutes the two solutions are compared, the colors equalized by diluting the darker, and the calculation made as explained under the estimation of nitrates.

The reactions consist in the conversion of the sulfanilic acid into diazobenzenesulfonic anhydrid, by the nitrite present; this compound is then in turn converted by the amidonaphthalene into azo-$\alpha$-amidonaphthalene-1-4-benzenesulfonic acid. The last-named body gives the color to the liquid.

## OXYGEN-CONSUMING POWER.

All organic materials being more or less easily oxidized, several methods have been suggested for determining the oxygen-consuming powers of waters by treatment with active oxidizing agents. These methods are, however, limited in value. The organic matters in water differ much in character and condition, and their oxidability is subject to much variation, according to the circumstances under which the test is made. Nevertheless, as a high oxygen-consuming power certainly indicates departure from purity, some additional evidence may be obtained. Potassium permanganate is especially suitable. The test is usually made by introducing a known amount of the permanganate into the water, which has been rendered acid, and measuring after a definite period the proportion which has been decomposed.

It must not be overlooked that if a water contains nitrites, ferrous compounds, or sulfur compounds other than sulfates, the proportion of oxygen consumed will be greater than that required for the organic matter. It has been proposed, in order to remove the nitrites before applying the permanganate, to take 500 c.c. of the water, add 10 c.c. of the dilute sulfuric acid, boil for twenty minutes, allow to cool, and then treat with permanganate. Since, however, the amount of nitrites, if appreciable, can be directly determined, it is more satisfactory to deduct from the oxygen consumed the amount required to convert the nitrites present into nitrates, and the remainder will be that required for the other oxidizable ingredients. Fourteen parts of nitrogen existing as nitrite require 16 parts of oxygen for conversion into nitrate. Similarly, 112 parts of iron in a ferrous compound will require 16 parts of oxygen for conversion to the ferric condition.

Of the following methods the first is due, in the main, to Tidy, has been improved by Dupré, and was approved by the Society of Public Analysts of Great Britain:

**Solutions Required:**

*Standard Permanganate.*—0.395 gram pure potassium permanganate is dissolved in distilled water, and the solution made up to 1000 c.c. One c.c. is equal to 0.0001 gram oxygen.

*Diluted Sulfuric Acid.*—Add 50 c.c. of pure sulfuric acid to 100 c.c. of water, and then add solution of potassium permanganate until a faint pink color is obtained, which is permanent when the liquid is heated to 80° F. for four hours.

*Potassium Iodid.*—Ten grams of the pure salt recrystallized from alcohol are dissolved in 100 c.c. of distilled water.

*Sodium Thiosulfate.*—One gram of the pure crystallized salt dissolved in 2000 c.c. of distilled water.

*Starch Indicator.*—One gram of clean starch is mixed smoothly with cold water into a thin paste, then poured gradually into about 200 c.c. of boiling water, the boiling continued for one minute, the liquid allowed to settle, and the clear portion used. It is best freshly prepared.

**Analytic Process:**

Two determinations are made—one, of the oxygen consumed in fifteen minutes, which is considered to represent the nitrites, sulfids, or ferrous compounds, and the other, of the oxygen consumed by four hours' action. Both determinations are made at a temperature of 80° F. Three glass-stoppered bottles, of about 350 c.c. capacity, are rinsed with strong sulfuric acid and then with water. In one is placed 250 c.c. of pure distilled water as a control experiment, and in each of the others 250 c.c. of the water to be tested. The bottles are stoppered and brought to a temperature of 80° F.; 10 c.c. of the dilute sulfuric acid and 10 c.c. of the standard permanganate are added to each, and the stoppers again replaced. At the end of fifteen minutes one sample of water is removed from the bath, and two or three drops of the potassium iodid solution added to remove the pink color. After thorough admixture, the thiosulfate solution is run in from a buret until the yellow color is nearly destroyed, a few drops of the starch solution added, and the addition of the thiosulfate continued until the blue color is quite discharged. If the addition of the thiosulfate solution has been properly conducted, one drop of the permanganate solution will restore the blue color.

The other bottles are maintained at 80° F. for four hours. Should the pink color disappear rapidly in the bottle containing the water under examination, 10 c.c. of the permanganate solution must be added to each bottle, in order to maintain a distinct pink color. At the end of four hours each bottle is removed from the bath, two or three drops of potassium iodid added, and the titration with thiosulfate solution conducted as just described. The calculation is most conveniently made as follows:

$a$ = number of c.c. required for the control experiment.
$b$ = number of c.c. required for the water under examination.
$c$ = available O in permanganate (0.001 for 10 c.c.).
$x$ = oxygen consumed by water.
Then, $a : a-b :: c : x$.

The following method was recommended by the Chemical Section of the American Association for the Advancement of Science:

"Prepare a solution of potassium permanganate containing 0.2 milligram of available oxygen to 1 c.c. and a solution of oxalic acid of such strength as to decompose the permanganate solution, volume for volume, the strength being redetermined from time to time. The water used for making these solutions should be purified by distillation from alkaline permanganate.

"To 200 c.c. of water to be examined, in a 400 c.c. flask, add 10 c.c. of dilute sulfuric acid (1: 3) and such measured quantity of the permanganate as will give a persistent color; boil ten minutes, add, if necessary, more permanganate in measured quantities, so as to maintain the red color; remove the flask from the lamp, add 10 c.c. of oxalic acid solution to destroy the color, or more if required by the excess of permanganate, and then add permanganate, drop by drop, until a faint pink tint appears. From the total quantity of permanganate used deduct the equivalent of the oxalic acid used, and from the remainder calculate the milligrams of oxygen consumed by the oxidizable organic matter in the water."

The oxygen-consuming power may also be indirectly estimated by the action of the organic matter upon silver compounds. H. Fleck's method depends upon the reduction produced by boiling the water with alkaline solution of silver thiosulfate and estimation of the unreduced silver. A. R. Leeds has proposed a method by treating the water with decinormal silver nitrate, exposing to light until it settles perfectly clear, and estimating the reduced silver.

These methods are open to practically the same objections as in the use of permanganate, and do not seem to possess any decided advantage. Qualitative results of some interest may occasionally be obtained by the following method: Two c.c. of a one per cent. solution of silver nitrate, rendered decidedly alkaline by ammonium hydroxid, are added to 100 c.c. of the water in a stoppered bottle, which is then placed in full sunlight for two hours. Waters containing but little organic matter will not show at the end of this period any appreciable tint.

## PHOSPHATES.

The following method is recommended by A. G. Woodman:

### Solutions Required:

*Ammonium Molybdate Solution.*—50 grams in 1 liter of distilled water.

*Nitric acid,* sp. gr. 107.

*Sodium Phosphate Solution.*—0.5324 gram crystallized disodium hydrogen phosphate, 100 c.c. of the above nitric acid, distilled water sufficient to make 1 liter. This is equivalent to 0.0001 $P_2O_5$ in 1 c.c.

### Analytic Process:

Fifty c.c. of the sample and 3 c.c. of nitric acid are evaporated to dryness in a porcelain dish on the water-bath, the residue heated for two hours at 100° C., and treated with 50 c.c. of cold distilled water added in several portions which are mixed in a comparison tube. It is usually unnecessary to filter. Four c.c. of the ammonium molybdate solution and 2 c.c. of nitric acid are added, the contents mixed, and after three minutes the color compared with that given by different quantities of the standard phosphate solution which have been made up to 50 c.c. and the reagents added in the same amount as above.

Blank tests must be made to determine the purity of the materials used. Distilled water kept for some time in glass vessels may contain appreciable amounts of substances giving color with the reagents.

Ammonium molybdate solution suitable for the gravimetric determination of phosphates may be prepared as follows:

Weigh into a beaker 10 grams of pure molybdenum teroxid, mix well with 40 c.c. cold distilled water, and add 8 c.c. strong ammonium hydroxid, sp. gr. 0.900. When completely dissolved, filter and pour slowly, with constant stirring, into a mixture of 40 c.c. of nitric acid, sp. gr. 1.42, and 60 c.c. of water. Add 0.005 gram sodium ammonium hydrogen phosphate, dissolved in a little water, agitate well, allow precipitate to settle twenty-four hours, and filter before using.

## DISSOLVED OXYGEN.

The method here given, a modification of Mohr's, was proposed by Blarez. It is rapid and satisfactory.

**Solutions Required:**

*Sodium Hydroxid.*—Forty grams of pure sodium hydroxid to the liter.

*Ferrous-ammonium Sulfate.*—Forty grams dissolved in about a liter of water, and acidified with a few drops of concentrated sulfuric acid.

*Decinormal Potassium Permanganate.*—3.156 grams dissolved in a liter of distilled water. The accuracy of this solution should be determined by titration with a known weight of ferrous-ammonium sulfate. One c.c. should be equivalent to 0.0392 gram ferrous ammonium sulfate (0.0008 gram of oxygen).

The apparatus employed (shown in Fig. 12) is a globular separator, of about 250 c.c. capacity. Above the bulb is a caoutchouc stopper carrying a cylindric funnel, of about 12 c.c. capacity, terminating in a tube, 8 mm. caliber, sharply contracted at the outlet to a capillary opening. The tube should project about 6 mm. below the stopper. The exact capacity of the apparatus is measured as follows: The bulb is completely filled with water and the stopper inserted; the level of the water will rise slightly in the funnel tube, and should be brought down to its outlet by drawing a little off at the stop-cock, after which the water is run into a graduated measure and its volume noted.

FIG. 12.

**Analytic Process:**

Thirty-five c.c. of mercury and ten c.c. of sodium hydroxid solution are put into the bulb, and then sufficient of the water to be tested to fill it. The funnel stopper is inserted, and the water which rises into the funnel brought into the bulb by cautiously running out at the stop-cock, mercury, the volume of which should be noted. The exact volume of water used is thus known. Five c.c. of the ferrous ammonium sulfate solution are poured into the funnel, brought into the bulb by running out mercury, and the liquid thoroughly mixed by giving the apparatus a gyratory movement. After standing five or six minutes, the oxygen will be completely absorbed; 10 c.c. of the diluted sulfuric acid are now added by the same method. On agitating the bulb, the contents become clear. The watery liquid is then transferred to a beaker and titrated with decinormal permanganate. A volume of water equal to that used in the test is poured into another beaker, 10 c.c. each of the sodium hydroxid and diluted sulfuric acid added, and then 5 c.c. of ferrous ammonium sulfate solution. The resulting liquid is titrated with permanganate. The weight of oxygen corresponding to the difference between the two titrations gives the weight of dissolved oxygen in the liquid employed.

Nitrates do not appear to impair the accuracy of this method, and the interfering action of nitrites and other reducing compounds is avoided by the control experiment.

It is perhaps hardly necessary to add that the exact temperature of the water is to be noted at the time of collection of the sample.

In transferring to the bulb, the water should be agitated as little as possible in contact with the air, in order to avoid the absorption of oxygen. A siphon should be used for this purpose, the lower end being allowed to reach to the bottom of the bulb.

## POISONOUS METALS.

Under this conventional title are included *barium*, *chromium*, *zinc*, *arsenic*, *copper*, and *lead*; *manganese*, *iron*, *aluminum*, also, though not usually classed in this group, are objectionable when present in notable amounts.

**Barium** is rarely present, and only in water containing no sulfates. It can be detected and estimated by slightly acidifying the water with hydrochloric acid, filtering if necessary, and adding solution of calcium sulfate. The precipitated barium sulfate is collected and weighed in the usual way.

**Chromium** is rarely present, but may be looked for in the waste waters of dye-works and similar sources. To detect it, a considerable volume of the water is evaporated to dryness with addition of a small amount of potassium chlorate and nitrate, transferred to a porcelain crucible and brought to quiet fusion; any chromium present will be found in the residue in the form of chromate. The fused mass, after cooling, is boiled with a little water, filtered, the filtrate rendered slightly acid with hydrochloric acid, and a solution of hydrogen dioxid added. In the presence of chromium a transient blue color will appear; by adding a little ether and shaking the mixture, the color will pass into the ether, and on standing will form a blue layer on the surface of the water.

**Zinc** is best detected by the test described by Allen. The water is rendered slightly alkaline by addition of ammonium hydroxid, heated to boiling, filtered, and the clear liquid treated with a few drops of potassium ferrocyanid; in the presence even of the merest trace of zinc a white precipitate will be produced.

**Arsenic** is most readily detected by Reinsch's test. One liter of the water is rendered slightly alkaline by pure sodium carbonate, and evaporated nearly to dryness in a porcelain basin. Two or three c.c. of water strongly acidulated with hydrochloric acid are placed in a small test-tube, about ½ of a square centimeter of bright copper foil is added, and the liquid boiled gently for a few moments. If the copper remains bright, showing that the reagents contain no arsenic, the water-residue is acidified with hydrochloric acid, added to the contents of the test-tube, and the liquid again boiled for several minutes. If arsenic be present, a steel-gray stain will appear on the copper. The slip is removed, washed with distilled water, *thoroughly* dried by pressure between filter paper, inserted into a narrow glass tube closed at one end, which has been previously dried by heating nearly to redness. The tube is gently heated at the point at which the copper rests; the deposit will sublime and collect on the cooler portion of the tube, in crystals which the microscope shows to be octahedral.

Since small amounts of arsenic frequently occur in reagents and in glass vessels, care must be taken to avoid such sources of error. Sodium carbonate solution may contain arsenic dissolved from the glass bottle in which it is kept. It is best, therefore, to use the solid carbonate for rendering the water alkaline, and to determine its purity before use.

**Iron** is detected by the addition of a drop of ammonium sulfid to the water in a tall, glass cylinder. Ferrous sulfid is formed, having a greenish-black color, instantly discharged by acidifying the water with dilute hydrochloric acid. A still better test is the production of a blood-red color, with potassium thiocyanate, due to the formation of ferric thiocyanate. The water should be first boiled with a few drops of nitric acid, to convert the iron to the ferric condition, cooled, and a drop or two of the solution of potassium thiocyanate added. The test is very delicate. Either of the above tests may be made quantitative by matching the color produced in 100 c.c. of the water with that obtained from a known weight of iron. The method with potassium thiocyanate is preferable, as it is more delicate and there are fewer interfering conditions. The following is the method as elaborated by Thompson and described in Sutton's "Volumetric Analysis":

**Solutions Required:**

*Standard Ferric Sulfate.*—0.7 gram ferrous ammonium sulfate is dissolved in water acidified with sulfuric acid, and potassium permanganate solution added until the solution turns a very faint pink color. The solution is diluted to a liter. One c.c. contains 0.1 milligram iron.

*Diluted Nitric Acid.*—Thirty c.c. concentrated nitric acid diluted with water to about 100 c.c.

*Potassium Thiocyanate.*—Five grams of the salt dissolved in about 100 c.c. water.

**Analytic Process:**

About 100 c.c. of the water are evaporated to small bulk, acidified with hydrochloric acid, and just sufficient dilute potassium permanganate solution added to convert all the iron to the ferric condition. The liquid is evaporated nearly to dryness to drive off excess of acid, then diluted to its original volume, 100 c.c. In two tall glasses marked at 100 c.c., 5 c.c. of the nitric acid and 15 c.c. of the thiocyanate solution are placed. To one of these a measured volume of the treated water is added and both vessels filled up to the mark with distilled water. If iron is present, a blood-red color will be produced. Standard iron solution is added to the second vessel until the color agrees. The amount of water which is added to the first glass will depend upon the quantity of iron it contains; not more should be used than will require two or three c.c. of the standard to match it, otherwise the color will be too deep for comparison.

**Manganese.**—The following method is described by Wanklyn in his treatise on water analysis. About one liter of the water is evaporated to small bulk, nearly neutralized by hydrochloric acid and treated with a few drops of a solution of hydrogen dioxid. The formation of a brown precipitate indicates the presence of manganese. The test is very delicate. The precipitate may be collected on a filter, the filter ashed, and the residue fused with a mixture of sodium carbonate and potassium nitrate. Green potassium manganate will be produced, which, when boiled with water, will give a bright-red solution of potassium permanganate. The quantitative determination is given elsewhere.

**Aluminum.**—Traces of this element are to be expected in all waters, and it is not usual to test for it except in elaborate analysis of the mineral ingredients, as described in another section. The use of aluminum sulfate as a coagulant in many rapid-filtration methods makes it necessary to examine effluents for excess of precipitant, and this may be done by the following method devised by Mrs. Richards:

To 25 c.c. of the water to be tested (concentrated from one liter or more, if necessary) is added a few drops of freshly prepared logwood decoction; any alkali is neutralized and the color is brightened by the addition of two or three drops of acetic acid. By comparison with standard solutions, the amount of alum present may be determined. One part of alum in 1,000,000 of water can be detected with certainty. In cases of greater dilution, concentration of several liters may be necessary to obtain a decisive test. The logwood chips yield the right color *only* after having been treated with boiling water *two or three times*, *rejecting* the successive decoctions. The first portion gives a yellow color, the third or fourth usually a deep red. The logwood chips must be fresh.

**Lead** may be readily detected by adding to the water in a tall glass cylinder a drop of ammonium sulfid; brownish-black lead sulfid is formed, which does not dissolve either by acidulating the water with dilute hydrochloric acid (distinction from iron), nor by the addition of about one c.c. of a strong solution of potassium cyanid (distinction from copper). S. Harvey gives the following method: 250 c.c. are placed in a precipitating jar, about 0.1 gram of crystallized potassium dichromate is added and dissolved by agitation. The same volume of lead-free water is treated in the same manner, and the two solutions placed side by side. Water containing 0.3 part per million will show a turbidity in fifteen minutes which will be rendered more distinct by contrast with the clear water alongside. By allowing the jar to stand for about twelve hours undisturbed, the precipitate will settle and will become still more distinct. No other metal likely to be present in water will give a similar reaction.

In the absence of copper the amount of lead present may be determined as follows: A solution is prepared containing 1.6 grams of lead nitrate to the liter; one c.c. of this contains one milligram lead. One hundred c.c. of the water to be tested are placed in a tall glass vessel, made acid by the addition of a few drops of acetic acid, and five c.c. of hydrogen sulfid added. In a similar vessel 100 c.c. of distilled water are placed, together with the same quantities of acetic acid and hydrogen sulfid, and sufficient of the standard lead solution to match the tint in the first cylinder. The amount of lead in the water under examination is thus known.

**Copper** is detected in the same manner as lead by acidifying the water with acetic acid and adding hydrogen sulfid. The precipitate is distinguished from lead sulfid by the fact that the color is discharged on the addition of about 1 c.c. of a strong solution of pure potassium cyanid. It may be further confirmed by the addition to another portion of the water of a solution of potassium ferrocyanid. In the presence of even a very small amount of copper, a mahogany-red color is produced.

In the absence of lead, copper is estimated in the same way as that metal, using, however, a standard solution of copper for the comparison liquid. This is made by dissolving 3.929 grams of crystallized copper sulfate in one liter of water. One c.c. of the solution contains one milligram copper.

If both lead and copper are present, a large quantity of the water should be evaporated to small bulk, and the metals separated and estimated by any one of the ordinary laboratory methods.

## BIOLOGIC EXAMINATIONS.

In a comprehensive sense the living organisms of water include representatives of all the great groups of animals and plants. The higher orders of organic forms are absent from very foul water. From an analytic point of view, observation is limited to the determinations of those forms which are inappreciable to the unassisted eye. So far as regards some of the moderately complex organisms, such as the minute crustaceans, algæ, desmids, and even the amebæ, it may be said that while some general inferences as to the character and history of the water may be deduced from an identification of the specific forms, no definite sanitary signification can be attached to them. From what is now known of the life-history of many parasitic organisms, it is evident that water that is freely accessible to any animal forms is liable to be dangerously polluted. Moreover, the dead bodies of such animals will furnish food to many forms of microbes and thus assist in the multiplication of the latter. The ova of the entozoa might in some cases be detected by careful search, and would indicate recent pollution of a highly dangerous character.

The number of the higher forms present in any sample will depend very much upon the point at which it is collected, they being more numerous in the neighborhood of large plants and at the bottom and sides of streams.

Several observers, notably Sedgwick and Rafter, have paid considerable attention to the recognition of the animal and vegetable forms in surface waters. Some of these forms cause disagreeable odors and colors; in the warm season of the year, when such water is stored in reservoirs, considerable annoyance is felt by the users, and the engineer-in-charge is subjected to much criticism. It has been found that even crude filtration methods, such as allowing the water to pass through a dike of porous soil before storing it in a reservoir, will diminish the tendency to these conditions. Cleansing a reservoir, disinfecting the inner surface, for instance, by whitewashing, has also improved the condition.

Observation, especially in Massachusetts, has shown that reservoirs intended for even moderately prolonged storage of water should be clean—that is, organic matter of any kind should not be allowed to accumulate on the bottom and sides. Drown states that while the water in one basin became foul from stagnation, in another which was carefully prepared by the removal of all soil and vegetable matter, and is supplied by a brown, swampy water from a district almost entirely free from pollution, the water is good at a depth of forty feet.

In Philadelphia, where large storage reservoirs are used for water that is often very muddy, but little trouble from the growth of microscopic organisms occurs. These reservoirs are artificial basins.

Sedgwick's method of collecting organisms other than microbes, with some modifications by Williston, is as follows:

In ordinary cases about 100 c.c. are employed. Sometimes it will be advantageous to use double this quantity, at other times much less. In rare cases the examination can be made upon unfiltered water. Originally sand was employed for a filter material, but Williston finds that precipitated silica, made by decomposing silicon fluorid with water, is more satisfactory. This precipitated silica is a commercial article, and its method of preparation is given in all the larger manuals of chemistry.

A small glass funnel with an even-calibered stem is selected, and the lower end of the stem plugged with a little absorbent cotton, upon which a layer three or four mm. deep of the filter-material is placed. The requisite volume of water is then allowed to filter through. The pledget of cotton is removed, and the filter-material is washed down with filtered or distilled water into a cell intended for microscopic examination. This cell is a glass plate accurately ruled, to which is attached a brass cell 50 mm. long by 10 mm. wide, of depth sufficient to hold about two c.c. of water. After the material has been allowed to distribute itself and settle in the cell, it is examined with a moderate power, and the different organisms in a varying number of the squares counted. Each organism may be counted by itself, if occurring in large numbers, the average of a few squares being sufficient for the purpose. Organisms less numerously represented may be counted by averaging a larger number of squares.

Filtering in this manner can not be relied upon in all cases. Indeed, in most cases the unfiltered water also should be examined. Some of the minute unicellular organisms pass readily through the small extent of sand or precipitated silica, or even through filter-paper.

It is not unlikely that the high-speed centrifugal apparatus now used in laboratories, associated with the employment of some fine precipitant, will aid in these investigations.

Dibdin prepares as follows, a "micro-filter," for the collection of minute suspended matters: A piece of combustion-tubing 20 to 25 cm. long is cleaned and drawn out in the middle to a capillary tube, and broken by a file scratch at a point at which the caliber is not more than two millimeters. Each of these pieces serves for a filter. A mixture of equal parts of air-dried clay and infusorial earth is made into a smooth, stiff paste with water and spread out on a slab in a layer about two millimeters deep. The capillary end of a tube is pressed down into the mass and moved in a circle until a plug is formed. This is warmed until dry, and heated to redness, forming a close filter.

The water to be examined is filtered in considerable amount,—one liter, for example, if there is but little suspended matter,—first through a hardened paper filter placed in a funnel, precautions being taken to exclude dust. The deposit is washed from the filter paper into the micro-filter by means of a jet of pure water. The suspended matter collects on the top of the clay plug and is measured by noting its height. If the clay plug is blocked the application of a filter-pump may be needed. When the column of water in the small tube is only about a centimeter in height, the main body of the tube is cut away by means of a file scratch and the deposit loosened from the filter plug, if necessary, by the use of a platinum wire. The tube is inverted so as to bring the deposit to the open end, and then cut off close to the plug. By this means the suspended matter is collected in a short capillary tube open at both ends. By gentle shaking, the contents may be brought onto a glass slide.

Owing to the great differences in the size of microscopic organisms, the mere enumeration of their numbers is not always an index of the amount of living matter in suspension. To obviate this, Whipple has suggested a standard unit of size, estimating by means of it the total volume of the organisms, and not their number. He finds by this method that the analytic and biologic results correspond much more closely than when mere numbers are recorded. The unit is an area of 400 microns—that is, a square of 20 microns on a side. The results are stated in number of standard units per cubic centimeter.

Mr. Whipple has investigated the conditions influencing the growth of the microscopic organisms in water. He finds that diatoms thrive best with a supply of nitrates and a free circulation of air; temperature alone has no very direct effect. Infusoria will be found in largest numbers when the water contains the greatest amount of finely divided organic matter. When the conditions bring about a circulation of the water, the organisms are not only brought constantly in contact with new food materials, but are enabled to reach the upper layers of the water where oxygen is abundant.

**Bacteriologic examinations** may be *qualitative* or *quantitative.* The former involves the determination of the species of microbes present, especially those having disease-producing power, or characteristic of some form of pollution. The processes are usually laborious, requiring extensive laboratory facilities. Quantitative examination—microbe-counting, as it may be called—is the determination of the number of microbes, or microbe-colonies, that can be grown from a given volume of water under specified conditions. As the growth of living organisms is influenced by all external conditions, the results of the culture of microbes are not comparable with one another, unless strict uniformity of methods has been observed. Neglect of this fact renders a very large part of the earlier work and some of the present-day work of little statistical value. Among the conditions materially affecting the growth of microbes are temperature, reaction of the culture-medium to different indicators, degree of exposure to light and air, and duration of cultivation. The composition of the culture-medium has much influence, and it is difficult to control this exactly, owing to the irregularity of quality of some of the materials used.

At the present day, microbe-counting for water analysis is done almost entirely with culture-media that are solid at ordinary temperatures but may be liquefied at or near blood-heat. Gelatin or agar is used for producing the solidity. The former is the most convenient, but its jelly melts at such a low temperature that it is of limited application, and agar is largely employed.

Apparatus for bacteriologic work is now all furnished of good quality by dealers, and will not need special description. For the ordinary methods of microbe-counting the following will be needed:

*Open-steam Sterilizer.* A modification of the Arnold sterilizer is now much used.

*Autoclave,* a closed-steam sterilizer, permitting the application of temperatures much above the boiling point of water.

*Hot Air Oven* for special sterilizations.

*Culture Oven,* with thermostat.

*Double Boiler* of agate or other good culinary ware. The inner vessel should have a capacity of a little more than a liter.

*Test-tubes,* about 12 cm. long and 1.5 cm. in diameter.

*Petri dishes,* about 10 cm. in diameter and 1.0 cm. deep. As far as possible, dishes of uniform size should be selected. Each dish and cover should be marked in the center by a diamond with a distinguishing number.

*Wire baskets* for holding several dozen test-tubes.

*Fermentation-tube,* such as used in the detection of sugar in urine.

*Ordinary laboratory appliances,* such as pipets, burets, funnels, beakers, and cotton-wool. Tin-foil cut in squares 5 cm. on the side.

The materials for preparing culture-media should be obtained from responsible dealers, who will furnish the grades regularly used. The following will assist in the selection.

*Gelatin.* A grade made in Germany and distinguished by a monogram of the initials WH is used.

*Agar.* A colorless grade is preferable.

*Peptone.* Witte's dry peptone is used.

*Glucose.* The grade termed "crystallized pure" is preferred; it consists principally of dextrose.

*Meat-extract.* That made by the Liebig Meat-Extract Company, limited, of London, is almost the only form used by bacteriologists, but there seems to be no reason for preference to some of the American extracts.

*Sodium chlorid.* A good quality of table salt will suffice.

*Glycerol* should be as free as possible from acid and mineral matters.

*Lactose* should be of high purity, especially free from milk-proteids.

**Preparation of Culture-media:**

*Bouillon* is the term applied to many forms of liquid media, prepared with meat juice or meat-extract. The ordinary bouillon is prepared according to the following formula:

Five hundred grams of finely-chopped meat, as free as possible from fat and gristle, are soaked overnight in about a liter of cold water, at a temperature between 0° C. and 10° C. The mass is then strained through a coarse towel and pressed until as much as possible of the liquid is obtained. To this is added 10 grams of peptone and 5 grams of common salt. It is then heated to boiling, best in the open-steam sterilizer, to coagulate albumin, after which it is filtered. The most difficult point in the work is neutralization. This is often accomplished by the use of sodium carbonate, which is added in small amounts until the liquid no longer affects red litmus paper. The better method is to titrate a portion of the bouillon with sodium hydroxid solution, and calculate from this the amount of that solution necessary to neutralize the whole of the liquid. Fuller has devised a good method of procedure. The bouillon is made up when cool to a definite volume, say 1000 c.c.; 5 c.c. are mixed with 45 c.c. of distilled water in a porcelain dish, boiled for three minutes, 1 c.c. of solution of phenolphthalein added, and quickly titrated with twentieth normal sodium hydroxid. The neutral point is the slight pink color not disappearing on gentle stirring. From the number of cubic centimeters used the amount of alkali needed to neutralize the whole solution is calculated, but this alkali should be added in the form of normal solution in order to avoid much dilution of the bouillon.

Bouillon may be modified in many ways, by the addition of different substances, but the inherent or possible acidity or alkalinity of these must be ascertained and corrected if culture results are to be kept standard.

A dextrose bouillon for special fermentation work is made by adding glucose in the proportion of 20 grams to 1000 c.c. of the liquid.

Meat-extract is often used instead of the infusion of chopped meat. Five grams of a good commercial extract are used for each 1000 c.c. of bouillon.

*Gelatin Media.*—The ingredients, other than the gelatin, are dissolved and treated as described in the making of bouillon. After neutralization, the gelatin is dissolved by gentle heating. If this contributes any acidity, it must be neutralized. The heating may be done in the double boiler. The liquid should not be heated strongly or for a long time, as the gelatinizing property may be injured. The solution is made up to the proper volume and filtered through paper.

*Meat-extract peptone-gelatin.*

| | | |
|---|---|---|
| Meat-extract, | 5.0 | grams |
| Peptone, | 10.0 | " |
| Gelatin, | 150.0 | " |
| Dextrose, | 2.0 | " |
| Sodium chlorid, | 5.0 | " |
| Water, | 1000.0 | c.c. |

The preparation of agar solution is more difficult than that of gelatin. Several methods have been suggested. Ravenel uses high pressure, according to the following methods:

*Preferable Method:*

| | | |
|---|---|---|
| (A) | Chopped meat, | 500 grams |
| | Water, | 500 c.c. |

These are mixed and allowed to stand overnight.

| | | |
|---|---|---|
| (B) | Agar, | 12 grams |
| | Water, | 500 c.c. |

Solution B is put into the autoclave, the pressure run up to 2 atmospheres, the heat withdrawn, and the boiler opened when the temperature has fallen a little below 100° C. The solution is allowed to cool to about 75° C. (below the coagulating point of albumin), 10 grams of dried peptone and 5 grams of sodium chlorid are added, A and B mixed, the liquid boiled for about three minutes, neutralized and filtered. The filtration is very quick—from ten to twelve minutes for a liter. A hot-water funnel is not needed, but the filter must be moistened with boiling water immediately before pouring in the agar. In the process with fresh meat the clarification is effected by the coagulation of the albumin in the meat-water, hence solution B must not be added to A until cool enough to avoid coagulation.

*Alternative method:*

| | | |
|---|---|---|
| (A) | Dried peptone, | 10 grams |
| | Common salt, | 5 " |
| | Meat-extract, | 5 " |
| | Water, | 500 c.c. |

Boil for three minutes and neutralize.

| | | |
|---|---|---|
| (B) | Agar-agar, | 12 grams |
| | Water, | 500 c.c. |

The agar is chopped fine and heated in the autoclave to two atmospheres. As soon as this pressure is reached, the heat is withdrawn and the liquid allowed to cool until below 100° C. before opening. The two solutions A and B are then mixed, cooled to 60° C., the whites of two eggs beaten in 50 c.c. of water added, well stirred in, and the whole then boiled and filtered through paper.

Instead of the white of egg, blood-serum may be used, which seems to add also to the nutritive value of the medium. Agar made with meat-extract will often form a precipitate during the sterilization.

Abbott gives the following method of preparing agar solution: The bouillon is prepared and neutralized in the usual way, then 15 grams of finely chopped agar are added, and water sufficient to make the volume 1250 c.c. The mass is boiled gently over a direct flame, stirring occasionally, for several hours. If the fluid goes below the liter level, enough water should be added to make up the amount. The boiling should be continued until about a liter is left in the vessel. When the solution of the agar is attained, the vessel is placed in a large dish of cold water, until it has cooled to about 70° C., the white of one egg that has been beaten up with water added, mixed well, and boiled again for a half-hour, avoiding the evaporation of the liquid below the liter point. The liquid is filtered through heavy folded filter paper at room-temperature. It is necessary that the solution should be not above 70° C. when the white of egg is added or it will become lumpy. Commercial egg-albumin in 10 per cent. solution in water may be used instead of white of egg. The solution thus prepared should filter rapidly.

*Potato Culture.*—Cultivation on potatoes has been much used as a method of distinguishing certain microbes. Large, sound potatoes should be selected, thoroughly washed, and cut into disks about five centimeters in diameter and one centimeter thick. These are placed in glass boxes (pomade boxes) which have lids with ground joint, and heated for about one-half hour in the sterilizer. Another method is to cut out cylinders with the aid of an apple-corer, or largest size cork-borer, slice these obliquely, and place them in test-tubes, which are then closed with cotton plugs and sterilized. The latter method does not give a large surface, but the growth of any inoculation may be easily watched.

Many special forms of culture-media are employed for bacteriologic investigations which do not come within the line of water analysis, and need not be described. One form is much employed in the search for the specific germ of typhoid fever, namely, Würtz's *litmus-lactose* solution. This may be with either agar or gelatin, in conjunction with meat extract. The nutrient medium must be made so as to possess such a degree of alkalinity that 10 c.c. will neutralize 0.5 c.c. of decinormal sulfuric acid. Lactose is added in the proportion of two or three grams to 100 c.c. of medium and the mixture sterilized, after which sufficient sterilized litmus tincture is added to give the fluid a distinct but not deep-blue color.

Cultivation in gelatin at ordinary temperatures usually yields a larger number of points of microbic life than in agar at blood-heat. This is due to the fact that many common water-bacteria do not grow well at the higher temperatures.

Culture-media when ready for use are distributed in test-tubes. These must be well cleaned. In laboratories in which regular chemical work is done the solution of crude chromic and sulfuric acids used for voltaic batteries is a good cleaning agent, the tubes being soaked in this for about a day, and then rinsed thoroughly and sterilized as noted below. In bacteriologic laboratories it is usual to cleanse the tubes with a 3 per cent. solution of sodium hydroxid. The tubes are boiled in the solution, rinsed, swabbed out with a brush, and allowed to dry in the inverted position. A cotton-wool plug is made for each tube, care being taken that it fits neatly, without creases or channels and not too tightly. The projecting part of the plug is clipped moderately close and a tinfoil cap placed on each. The arrangement is sterilized in the hot-air oven at 150° C. When cold, the tinfoil and plug are carefully removed, about 10 c.c. of culture-medium put into each tube, with as little outside contamination as possible, the plug and cap replaced, and the tubes and contents sterilized in the open-steam sterilizer. The wire baskets are used to hold the tubes during the sterilizations.

For making cultures definite volumes of the water sample are introduced into the culture-medium, and if this is a solidifying form, it is put into the Petri dish. All the manipulations must be conducted with great care to avoid contamination. When there is no clue to the amount of microbes present, it will be necessary to make cultures with different proportions of water. Some tubes may be inoculated with a few drops, some with three to five drops, and some with 1 c.c. Some operators dilute the water considerably and take small measured volumes. If this method is used, the diluting water must be distilled and have been well sterilized, by at least five minutes' boiling, and cooled out of contact of air. All pipets, dishes, and other apparatus that come in contact with the water must have been first sterilized.

The test-tubes containing the culture-medium are warmed gently, just enough to render the culture-medium fluid, the desired volume of the water added, the mixture shaken and promptly poured into the Petri dishes, covered and placed in the oven, which should have been already raised to the temperature at which it is desired to conduct the work. Unless specially desired otherwise, cultures should be made in the dark. They may be made at any temperature short of that at which the medium melts, but either ordinary temperature or 37° C. is usually selected. The condition of the plates should be observed at intervals of twenty-four hours, and the points of microbic life counted and recorded. After some days the growth will become so luxuriant or the liquefaction of the medium so extensive that accurate observation is not possible.

If the microbic points are numerous, it will be necessary to employ a counting scale. For the Petri dish, Pake's modification of Lafar's scale is cheap and sufficient.

**General Character of the Microbes in Natural Waters.**—The microörganisms of natural waters are principally included in the genera *Bacillus* and *Spirillum*, especially the former. Micrococci and molds are rare, and are generally due to contamination by dust.

Microbes are distinguished according to the conditions favorable to their growth, as follows:

| | |
|---|---|
| Saprophytic. | Growing on dead matter. |
| Parasitic. | Growing only on living matter. |
| Aërobic. | Requiring free oxygen. |
| Anaërobic. | Not requiring free oxygen. |

When the organism possesses the power of adapting itself to different conditions, the term *facultative* is applied; when it can grow only under special conditions, the term *obligatory* is applied.

Microbes are also differentiated by the effect which they produce upon the culture-medium. Some species rapidly or slowly liquefy the jelly with evolution of foul-smelling gases; others—chromogenic microbes—produce characteristic colors. Many do not produce any positive modification, and for purposes of distinction it is usual to transfer portions of the colonies to other culture-media. Such special cultures are obtained by taking up a portion of the colony on the end of a wire which has been just sterilized by heating to redness and inoculating the prepared medium.

*Indol Reaction.*—Indol, $C_8H_7N$, more properly indin, is a weak base, which is a product of the growth of many species of microbes, and the detection of it may, therefore, be utilized as a differentiation test. Kitasato gives the following method for performing the test:

Ten c.c. of an alkaline-peptone-meat infusion (without gelatin), which has been previously inoculated with the microbes to be tested, and kept for twenty-four hours at blood-heat, are treated with 1 c.c. of solution of pure potassium nitrite (0.02 gram in 100 c.c.) and then with a few drops of concentrated sulfuric acid. In the presence of indol a rose or deep-red color is developed. *Spirillum choleræ* and *Bacillus coli communis* give the reaction strongly; *S. Finkleri* feebly; the so-called *B. typhosus* ordinarily does not give it.

Careful and experienced bacteriologists do not now claim to be able to isolate the typhoid bacillus from natural waters. The effort has failed even with waters that are obviously polluted. In default of a method for such detection, resort is had to methods for the detection of the microbe known as *Bacillus coli communis.* This being a constant inhabitant of the intestinal canal of the highest animals, and being almost always associated with dangerous pollution, the detection of it in water indicates previous contamination. This organism is not constant in character, but, in common with many other dangerous microbes, grows well at blood-heat, while many common water, air, and soil organisms do not. Some mild germicides also affect the latter class of microbes more than the intestinal bacilli. Upon these principles have been founded many methods for differentiation, two of which are in common use.

The Franklands, after reviewing at length the various methods that have been suggested for differentiating the typhoid bacillus, show that most of them are quite insufficient. A routine treatment is, however; suggested as follows:

The water is freed from the ordinary water-bacteria by preliminary culture in Parietti's solution. This is a phenol-broth prepared by mixing 10 c.c. of neutral bouillon with 0.25 c.c. of the following solution:

| | | |
|---|---|---|
| Phenol, | 5 | grams |
| Hydrochloric acid, | 4 | " |
| Water, | 100 | " |

This solution is sterilized by heating it for twenty-four hours at 37° C. The tubes are then inoculated with from one to ten drops of the water sample, which must be thoroughly mixed with the broth, and again kept in the sterilizer for not less than forty-eight hours. If any of the tubes appear turbid after the treatment they should be submitted to plate cultivation, and any colonies which resemble those produced by the typhoid bacillus should be further studied by inoculation into gelatin tubes to observe the gas-producing test, into milk to note if coagulation occurs, and by cultivation in broth to determine if indol-reaction will be obtained.

The method of Theobald Smith is to cultivate the water sample at blood-heat with a bouillon rich in dextrose and note whether there is evolution of gas. The fermentation tube is used. Sufficient bouillon is put in to fill the upright stem and the curved part, but not much of the bulb. The whole is then well sterilized in the open steam sterilizer, a cotton plug with tinfoil cover having been previously placed in the opening of the bulb. The apparatus is cooled; a few drops of the water sample are then introduced into the bouillon, taking care not to allow outside contamination, the plug and tinfoil are replaced, and the tube kept at 37° C. for about forty hours. An accumulation of gas at the top of the tube indicates that microbes of the type of the *B. coli communis* are present. Several tubes and one or two control tubes, that is, tubes which are not inoculated with water, should be tried together. Portions of the gas-producing bouillon may be inoculated into sterile agar and cultivated at the same temperature after pouring into the Petri dish.

The bouillon is made according to the procedure on page 76, except that 20 grams of glucose are used to the liter.

The resemblance between the two forms, *B. typhosus* and *B. coli communis*, is so great, and the variability of both forms so marked, that some observers have suggested that they are but varieties of the same specific bacillus. Much attention has been paid to the distinctions. The following synopsis has been given by Abbott:

| CHARACTERISTICS. | B. TYPHOSUS. | B. COLI COMMUNIS. |
|---|---|---|
| Motility, | Conspicuous. | Not marked. |
| Growth in gelatin, | Slow. | Not very slow. |
| " " potato, | Usually inconspicuous. | Always rapid and visible. |
| " " milk, | No coagulation; no acidity. | Acidity and coagulations in forty-eight hours in incubator at 38° C. |
| Growth in media containing glucose, lactose, or sucrose, | No evolution of gas. | Marked evolution of gas. |
| Growth in media containing lactose and litmus, | Colonies pale blue; no reddening of surrounding medium. | Colonies pink; surrounding medium red. |
| Indol reaction in peptone solution (forty-eight hours at 38° C.) | Rarely present. | Always present. |

It will be seen that the characteristics of *B. typhosus* are rather negative than positive. The data are derived from cultures obtained from intestinal discharges or viscera of patients affected with typical typhoid fever.

## TECHNIC EXAMINATIONS.

### GENERAL QUANTITATIVE ANALYSIS.

**Silica, Iron, Aluminum, Manganese, Calcium, and Magnesium.**—One liter of the water acidified with hydrochloric acid is evaporated to complete dryness, best in a platinum dish, the residue treated with hydrochloric acid and water, and the separated *silica* filtered, washed, dried, ignited in a platinum crucible, and weighed.

To the filtrate, previously boiled with a few drops of strong nitric acid, slight excess of ammonium hydroxid is added, the liquid boiled several minutes, the precipitate collected, washed thoroughly with boiling water, dried, ignited, and weighed. It consists of $Fe_2O_3$ and $Al_2O_3$. It also contains all the phosphates and some manganese if much is present in the water. In such cases the precipitate before drying is redissolved in hydrochloric acid and neutralized with a dilute solution of ammonium carbonate until the water becomes almost turbid. It is then boiled, and the precipitate, now free from manganese, washed, dried, ignited, and weighed. The iron may be determined by dissolving the precipitate in strong hydrochloric acid and employing the colorimetric method described on page 66.

If no manganese or only traces are present, the filtrate from the iron is mixed with sufficient ammonium chlorid to prevent the precipitation of the magnesium, ammonium hydroxid, and then ammonium oxalate added in quantity sufficient to precipitate the calcium and to convert all the magnesium into oxalate, and thus hold it in solution. The precipitate contains all the calcium and some of the magnesium. If the magnesium is present only in relatively small quantity, the amount carried down may be disregarded; otherwise a second precipitation should be made as follows: The solution is allowed to stand until the precipitate has subsided; this will require some hours. The supernatant liquid is poured off through a filter, the precipitate washed by decantation, then dissolved in hydrochloric acid, water added, then ammonium hydroxid and a small quantity of ammonium oxalate. After the calcium oxalate has thoroughly subsided it is filtered off, washed, and dried. If quite small in amount, it is placed with the filter in a weighed platinum crucible, ignited over the Bunsen burner for a short time, and then over the blast lamp for from five to fifteen minutes. The calcium is thus obtained in the form of oxid, which is allowed to cool in the desiccator and weighed. The weight thus obtained multiplied by 0.714 gives the weight of *calcium*. When the amount of precipitate is large, it is better to remove it from the filter, and heat it just short of redness until it assumes a grayish tint. It then consists of calcium carbonate. To this is added the ash of the filter. The weight of the calcium carbonate multiplied by 0.4 gives the weight of calcium.

The calcium may be determined by titration. The precipitate of calcium oxalate, after thorough washing, is dissolved from the filter by warm, dilute, sulfuric acid, heated to about 65° C., and titrated with decinormal permanganate until a pink tint is obtained. One c.c. of the permanganate is equivalent to 0.0020 calcium; 0.0028 calcium oxid; 0.0050 calcium carbonate.

The filtrates are mixed, slightly acidified with hydrochloric acid, concentrated and cooled, ammonium hydroxid and sodium phosphate added in excess, stirred briskly and allowed to stand in the cold for about twelve hours. The precipitated ammonium magnesium phosphate is brought upon a filter, that adhering to the sides of the vessel being dislodged by rubbing with a glass rod tipped with a piece of clean rubber tubing. It is washed with a solution made by mixing one part of the ammonium hydroxid of 0.96 sp. gr. with three parts of water. The precipitate is dried, transferred to a platinum crucible, the filter ashed separately and added to it, and the whole heated at first gently and then to intense redness for several minutes. After cooling, it is weighed. It consists of magnesium pyrophosphate; the weight multiplied by 0.218 gives the weight of *magnesium.*

Manganese, if present in appreciable quantity, is separated before the precipitation of the calcium, as follows: The filtrate from the iron precipitate is slightly acidulated with hydrochloric acid, concentrated, and the manganese precipitated as sulfid by colorless or slightly yellow solution of ammonium sulfid. The flask, which should be nearly full, is stoppered, allowed to rest in a moderately warm place until the precipitate has thoroughly settled, filtered, washed with dilute ammonium sulfid water, and purified by dissolving in a small quantity of hydrochloric acid and reprecipitating with ammonium sulfid. It is filtered off, washed as before, dried, placed in a weighed porcelain crucible, covered with a little sulfur, and ignited in a current of hydrogen introduced into the crucible by a tube passing through a hole in the cover. The pure manganese sulfid thus obtained is allowed to cool and weighed. The weight multiplied by 0.633 gives *manganese.*

**Sulfates.**—Five hundred c.c. of the clear water are slightly acidulated with hydrochloric acid, heated to boiling, and barium chlorid solution added in moderate excess. The precipitated barium sulfate is allowed to subside completely, collected upon a filter, washed thoroughly, dried, and incinerated. The weight multiplied by 0.411 gives $SO_4$. If the proportion is very low, it will be advisable to concentrate the water to one-fifth or one-tenth its bulk before precipitating.

**Control. Potassium, Sodium, and Lithium.**—From 250 to 1000 c.c. of the water, according to the amount of solid matters present, are evaporated to dryness in a platinum dish, and the residue treated with a small amount of water and sufficient dilute sulfuric acid to decompose the salts present. The dish should then be covered and placed upon the water-bath for five or ten minutes, after which any liquid spurted on the cover is washed into the dish, the whole evaporated to dryness and heated to redness. A few drops of ammonium carbonate solution should then be mixed with the residue, and the ignition repeated to insure the removal of the last portions of free acid. In the majority of cases the only basic elements present in considerable quantity are calcium, magnesium, and sodium. The *sodium* may be determined indirectly, therefore, by calculating from the amount of calcium and magnesium found, the calcium and magnesium sulfate in the residue, and subtracting this sum, together with the silica, from the total residue.

For the determination of potassium and sodium in ordinary well and river waters, not less than two liters should be employed. When lithium is to be determined, it is generally necessary to use much more. In any case, as the alkalies are to be weighed as chlorids, it is advisable, if notable amounts of sulfates are present, to precipitate them by addition of barium chlorid.

The water is evaporated to about 200 c.c., a slight excess of calcium hydroxid added to the hot liquid,—generally three c.c. of thin milk of lime will be sufficient,—and the heat continued for several minutes. It is then washed into a 250 c.c. flask, disregarding the insoluble portion adhering to the dish, which, however, should be thoroughly washed, and the washings added to the flask. After cooling, the flask is filled up to the mark with distilled water, thoroughly mixed, the precipitate allowed to settle, and the liquid filtered through a dry filter. Two hundred c.c. of the filtrate are measured into another 250 c.c. flask, ammonium carbonate and ammonium oxalate added, filled with water up to the mark, mixed, allowed to settle, filtered through a dry filter, 200 c.c. of the filtrate measured off, and evaporated to *thorough dryness* in a platinum crucible, heating very cautiously at the last stages, to avoid loss by spurting. The low-temperature burner is suited for this purpose. The crucible is now covered and cautiously heated to dull redness, cooled, and weighed. The residue contains the potassium, lithium, and sodium as chlorids. It contains, sometimes, also, traces of magnesium, which may be removed by treating again with lime and ammonium carbonate and oxalate. It is frequently of advantage, in evaporating these saline solutions, to add, when the solution becomes concentrated, several cubic centimeters of strong hydrochloric acid. This precipitates the greater portion of the salts in a finely granular condition, and renders loss by spurting less liable to occur.

If potassium and sodium chlorids only are present, the residue is dissolved in a small quantity of water, an excess of a concentrated neutral solution of platinum chlorid added, evaporated to small bulk at a low heat on the water-bath, some eighty per cent. alcohol added, allowed to stand, the clear liquid decanted off on a small filter, and the residue washed in this way several times by fresh, small portions of eighty per cent. alcohol. The precipitate is then washed on to the filter with alcohol, washed again with eighty per cent. alcohol, thoroughly dried and transferred as far as possible to a watch-glass. The small portion on the filter is dissolved off and the solution placed in a weighed platinum dish and evaporated to dryness. The main portion on the watch-glass is then added, and the whole dried to a constant weight at about 260° F., cooled, and weighed. The weight thus found multiplied by 0.3 gives the weight of *potassium chlorid.* This subtracted from the combined weight of the chlorids gives the weight of *sodium chlorid.*

Lithium, if present, is best separated before the treatment with platinum chlorid. The following method, devised by Gooch, gives good results: To the concentrated solution of the weighed chlorids, amyl alcohol is added and heat applied, gently at first, to avoid bumping, until the water disappears from the solution and the point of ebullition becomes constant at a temperature which is approximately that at which the alcohol boils (270° F.), the potassium and sodium chlorids are deposited, and the lithium chlorid is dehydrated and taken into solution. The liquid is then cooled, and a drop or two of strong hydrochloric acid added to reconvert traces of lithium hydroxid in the deposit and the boiling continued until the alcohol is again free from water. If the amount of lithium chlorid be small, it will be found in the solution and the potassium chlorid and sodium chlorid in the residue, excepting traces which can be allowed for. If the lithium chlorid exceed ten or twenty milligrams, the liquid may be decanted, the residue washed with amyl alcohol, dissolved in a few drops of water, and treated as before. For washing, amyl alcohol, previously dehydrated by boiling, is to be used and the filtrates are to be measured apart from the washings. In filtering, the Gooch filter with asbestos felt may be used with advantage, applying gentle pressure by the aid of the filter-pump. The crucible and residue are ready for weighing after gentle heating over the low-temperature burner. The weight of the insoluble chlorids is to be corrected by adding 0.00041 for every 10 c.c. of amyl alcohol in the filtrate, exclusive of the washings, if only sodium chlorid be present; 0.00051 for every 10 c.c. if only potassium chlorid, and 0.00092 in the presence of both these chlorids.

The filtrate and washings are evaporated to dryness in a platinum crucible heated with sulfuric acid, the excess driven off, and the residue ignited to fusion, cooled, and weighed. From the weight is to be subtracted, for each 10 c.c. of filtrate, 0.0005, 0.00059, or 0.00109, according as only sodium chlorid, potassium chlorid, or both were present in the original mixture.

**Hydrogen Sulfid.**—The following method is taken from Sutton's "Volumetric Analysis":

**Reagents Required:**

*Centinormal Iodin.*—Dry, commercial iodin is intimately mixed with one-fourth its weight of pure potassium iodid and gently heated between two clock-glasses by resting the lower on a hot plate. The iodin sublimes in a perfectly pure condition. It is allowed to cool under the desiccator, 1.269 grams weighed out, together with 1.8 grams of pure potassium iodid, dissolved in about 50 c.c. of water, and the solution made up exactly to a liter. The liquid must not be heated, and care should be taken that no iodin vapor is lost. One c.c. is equivalent to 0.00017 $H_2S$. The solution is best prepared in stoppered bottles, which should be completely filled and kept in the dark. It will not even then keep very long, and should be standardized by titration with a weighed amount of pure sodium thiosulfate, which should be powdered previous to weighing, and pressed between filter-paper to absorb any moisture. Fifty c.c. of the iodin solution, when of full strength, will require 0.124 gram of sodium thiosulfate.

*Starch Indicator.*—See page 57.

**Analytic Process:**

Ten c.c., or any other necessary volume of the iodin solution, is measured into a 500 c.c. flask, and the water to be examined added until the color disappears. Five c.c. of starch liquor are then added, and the iodin solution run in until the blue copper appears; the flask is then filled to the mark with distilled water. The respective volumes of iodin and starch solution, together with the added water, deducted from the 500 c.c., will show the volume of water actually titrated by iodin. A correction should be made as follows for the excess of iodin required to produce the blue color: Five c.c. starch solution are made up with distilled water to 500 c.c., iodin run in until the color matches that in the test, and the volume of iodin solution so used subtracted from the figure obtained in the first titration.

**Hardness. $CO_3$ in Normal Carbonates.**—Waters containing considerable quantities of calcium and magnesium are said to be hard. Since the solution of calcium and magnesium carbonate in water depends partly upon the presence of carbon dioxid, boiling precipitates the greater portion of the carbonates, the result being to diminish the hardness—*i. e.*, to soften the water. Magnesium and calcium sulfates and chlorids are not precipitated in this way. Hardness, therefore, is divided into two classes, temporary and permanent, the former being that which may be removed by boiling. The determination may be made either by titration or by soap solution.

TITRATION METHOD.—This method is due to Hehner.

**Reagents Required:**

*Standard Sodium Carbonate.*—1.06 grams of recently ignited pure sodium carbonate are dissolved in water and the solution diluted to 1000 c.c. One c.c. = 0.00106 gram $Na_2CO_3$ equivalent to 0.001 gram $CaCO_3$.

*Standard Sulfuric Acid.*—One c.c. of pure concentrated sulfuric acid is added to about 1000 c.c. of water. Fifty c.c. of the standard sodium carbonate are placed in a porcelain dish, heated to boiling, a few drops of a solution of methyl orange added, and the sulfuric acid cautiously run in from a buret until the proper change of color occurs. From the figure thus obtained, the extent to which the acid should be diluted in order to make 1 c.c. of the sodium carbonate equivalent to 1 c.c. of the acid may be calculated. The proper amount of water is then added, and the solution verified by again titrating.

**Analytic Process:**

*Temporary Hardness.*—One hundred c.c. to 250 c.c. of the water tinted with the indicator are heated to boiling, and the sulfuric acid cautiously run in until the color-change occurs. Each cubic centimeter required will represent one part of calcium carbonate or its equivalent per 100,000 parts of the water.

*Permanent Hardness.*—To 100 c.c. of the water is added an amount of the sodium carbonate solution more than sufficient to decompose the calcium and magnesium sulfates, chlorids, and nitrates present; usually a bulk equal to the water taken will be more than sufficient. The mixture is evaporated to dryness in a nickel or platinum dish, and the residue extracted with distilled water. The solution is filtered through a very small filter, and the filtrate and washings titrated hot with sulfuric acid as above; or 25 c.c. of distilled water may be poured on the residue, and the solution obtained filtered through a dry filter, the filtrate measured and titrated. The difference between the number of cubic centimeters of sodium carbonate used and the acid required for the residue will give the permanent hardness.

If the water contains sodium or potassium carbonate, there will be no permanent hardness, and there will be more acid required for the filtrate than the equivalent of the sodium carbonate added. From this excess the quantity of sodium carbonate in the water may be determined.

Since any alkali carbonate in the water would be erroneously calculated as temporary hardness by the direct titration, the equivalent, in terms of calcium carbonate, of the alkali carbonate present should be deducted from the figure given by the titration in order to get the true temporary hardness.

The total $CO_3$ in normal carbonates is given by the direct titration of the water with dilute sulfuric acid. One c.c. of the acid is equivalent to 0.0006 gram of $CO_3$.

Soap Method.—Many chemists estimate hardness by the use of soap solution. The following is a description of this method, as carried out in the laboratory of the Massachusetts State Board of Health:

**Reagents Required:**

*Standard Calcium Chlorid Solution.*—0.2 gram of Iceland spar is dissolved in dilute hydrochloric acid in a porcelain dish, the solution evaporated to dryness, redissolved and reëvaporated, until a perfectly neutral salt remains. This is dissolved in water and made up to one liter. One c.c. contains calcium equivalent to 0.0002 gram calcium carbonate.

*Soap Solution.*—0.50 gram of best quality, dry, white, Castile soap is cut into thin shavings, dissolved in a mixture of 250 c.c. of 96 per cent. alcohol and 250 c.c. of distilled water, and allowed to stand overnight to settle; 50 c.c. of the clear liquid are then made up to one liter, enough alcohol being used to keep all of the soap in solution. Fifty c.c. of the standard solution of calcium chlorid, which, according to the table, should take exactly 14.25 c.c. of standard soap, are used to test the strength. The soap solution thus prepared does not change perceptibly if air has no access to it, and, if used with a siphon buret attached to the bottle, will keep for five or six weeks or longer. It contains 5.2 grams of Castile soap to the liter.

For the standardization of the soap, and for the determination of the hardness of any water, 50 c.c. of the sample or of the standard calcium chlorid solution are placed in a flask or bottle of 200 c.c. capacity, and of a convenient shape, and the soap solution added, $\frac{2}{10}$ or $\frac{3}{10}$ of a c.c. at a time, shaking well after each addition, until a lather is obtained which is permanent for five minutes and covers the entire surface of the liquid with the bottle placed on its side.

The following table gives the hardness corresponding to the number of cubic centimeters of soap solution used in the analyses:

| C.c. of Soap Solution. | Hardness. | C.c. of Soap Solution. | Hardness. | C.c. of Soap Solution. | Hardness. |
|---|---|---|---|---|---|
| 0.7 | 0.0 | 3.7 | 4.1 | 6.7 | 8.4 |
| 0.8 | 0.1 | 3.8 | 4.2 | 6.8 | 8.5 |
| 0.9 | 0.3 | 3.9 | 4.4 | 6.9 | 8.7 |
| 1.0 | 0.4 | 4.0 | 4.5 | 7.0 | 8.8 |
| 1.1 | 0.6 | 4.1 | 4.7 | 7.1 | 9.0 |
| 1.2 | 0.7 | 4.2 | 4.8 | 7.2 | 9.1 |
| 1.3 | 0.9 | 4.3 | 5.0 | 7.3 | 9.2 |
| 1.4 | 1.1 | 4.4 | 5.1 | 7.4 | 9.4 |
| 1.5 | 1.2 | 4.5 | 5.2 | 7.5 | 9.5 |
| 1.6 | 1.4 | 4.6 | 5.4 | 7.6 | 9.7 |
| 1.7 | 1.5 | 4.7 | 5.5 | 7.7 | 9.8 |
| 1.8 | 1.6 | 4.8 | 5.7 | 7.8 | 10.0 |
| 1.9 | 1.8 | 4.9 | 5.8 | 7.9 | 10.1 |
| 2.0 | 1.9 | 5.0 | 6.0 | 8.0 | 10.3 |
| 2.1 | 2.0 | 5.1 | 6.1 | 8.1 | 10.4 |
| 2.2 | 2.2 | 5.2 | 6.2 | 8.2 | 10.6 |
| 2.3 | 2.3 | 5.3 | 6.4 | 8.3 | 10.7 |
| 2.4 | 2.4 | 5.4 | 6.5 | 8.4 | 10.9 |
| 2.5 | 2.6 | 5.5 | 6.7 | 8.5 | 11.0 |
| 2.6 | 2.7 | 5.6 | 6.8 | 8.6 | 11.2 |
| 2.7 | 2.8 | 5.7 | 7.0 | 8.7 | 11.3 |
| 2.8 | 2.9 | 5.8 | 7.1 | 8.8 | 11.5 |
| 2.9 | 3.1 | 5.9 | 7.2 | 8.9 | 11.6 |
| 3.0 | 3.2 | 6.0 | 7.4 | 9.0 | 11.8 |
| 3.1 | 3.3 | 6.1 | 7.5 | 9.1 | 11.9 |
| 3.2 | 3.5 | 6.2 | 7.7 | 9.2 | 12.1 |
| 3.3 | 3.6 | 6.3 | 7.8 | 9.3 | 12.2 |
| 3.4 | 3.7 | 6.4 | 8.0 | 9.4 | 12.4 |
| 3.5 | 3.9 | 6.5 | 8.1 | 9.5 | 12.5 |
| 3.6 | 4.0 | 6.6 | 8.2 | | |

The soap solution must be added in small quantities, especially in the presence of magnesium compounds. If much carbonic acid be liberated, it is well to remove it by suction. The table given above does not apply to hardness above 12.5. If the water tested requires more than

10 c.c. of the standard soap solution, a smaller portion of 25 c.c., 10 c.c., or even 2 c.c., as the case may require, is measured out and made up to a volume of 50 c.c. with recently distilled water. This will keep the results comparable with each other, although the dilution introduces some error into the calculation.

If the hardness of a water is given as 9.0, it means that in 100,000 pounds of water there is of calcium and magnesium salts a quantity which gives the same hardness to water which would be given by nine pounds of calcium carbonate. In order to soften this water for manufacturing purposes, about nine pounds of soda ash will be required, and for laundry purposes about ninety pounds of soap.

**Free and Half-bound Carbonic Acid.**—Several methods for the determination of these data have been devised. Pettenkofer's is much used, but F. B. Forbes and G. H. Pratt, after careful study of different methods, favor the Lunge-Trillich (also termed the Seyler) method, which they describe as follows:

One hundred c.c. of the sample are placed in a tall glass cylinder, by means of a siphon (in order to avoid contact with air), 6 drops of neutral alcoholic solution of phenolphthalein added, and $\frac{N}{50}$ sodium carbonate run in from a buret with careful stirring, until a faint permanent pink is obtained. If the water contains much free carbonic acid, it is better to take less than 100 c.c., and in every case care must be taken not to stir the sample so vigorously as to cause loss of the acid, nor to proceed so slowly that it may be absorbed from the air. The solutions must be carefully standardized and preserved so that they do not absorb the acid. The fixed carbonic acid is determined on another portion of the sample by Hehner's method as given above. In waters acid to phenolphthalein this will be equal to the half-bound.

When the water is alkaline to phenolphthalein, the alkalinity with this indicator is first determined, then the total alkalinity by Hehner's method. Twice the phenolphthalein alkalinity subtracted from the total alkalinity gives the half-bound acid, no free acid being present in this case, and the half-bound being less than the fixed. If the water is neutral to phenolphthalein, the half-bound may be equal to the fixed.

Forbes and Pratt have modified the Pettenkofer methods as follows:

Ground glass-stoppered bottles, holding approximately 480 c.c., are accurately calibrated by weighing completely filled with water. The bottle is filled with the water to be analyzed by means of a siphon, the glass stopper inserted, leaving no air-bubble, and the neck of the bottle wiped dry. The glass stopper is then carefully removed, and the 57 c.c. of the water withdrawn by means of an accurately calibrated pipet, in order to make room for the reagents. Three c.c. of strong barium chlorid solution (8 grams per liter), 2 c.c. of saturated ammonium chlorid solution, and 50 c.c. of standard barium hydroxid are then introduced, the bottle quickly stoppered, well shaken, and set aside to settle.

There is now in the bottle an air space of only 2 c.c., which is left to avoid the possibility of loss of liquid when the stopper is inserted. After the precipitated carbonates have completely settled out, several portions of 100 c.c. are siphoned off and titrated with $\frac{N}{50}$ sulfuric acid, which is prepared from decinormal acid, against which the barium hydroxid is standardized, by carefully diluting with water freed from carbonic acid by boiling. The barium hydroxid that we use is approximately $\frac{N}{15}$, and is carefully preserved out of contact with the air, the bottle in which it is kept being fitted with an arrangement whereby the air is drawn through soda-lime before entering either the bottle or the buret. The figure obtained by averaging several results of titration of portions of 100 c.c. is taken as the true value.

The use of this large quantity of water and the titration of 100 c.c. portions reduce considerably the errors due to the difficulty of obtaining the exact end-point, and those due to inaccuracies of measurement.

**Boric Acid.**—To detect it, add to one liter of the water sufficient sodium carbonate to render it distinctly alkaline. Evaporate to dryness, acidify with hydrochloric acid, moisten a slip of turmeric paper with the liquid, and dry it at a moderate heat. In the presence of boric acid the paper will assume a distinct brown-red tint.

**Analysis of Boiler Scale.**—If the scale is made up of pieces of decidedly different quality, some being hard and gritty, others soft and friable, separate tests should be made on representative samples of each sort; but if the general character is fairly uniform, it will be sufficient to sample the entire mass and reduce about 5 grams to a fine powder, finishing in an agate mortar. All of the quantity selected as the sample should be equally finely powdered.

0.5 gram should be heated in a covered beaker with moderately strong hydrochloric acid, until all soluble matter is dissolved; the liquid is then evaporated to dryness on the water-bath, redissolved in water containing some hydrochloric acid, and filtered. The precipitate is silica. The filtrate and washings are mixed and divided into convenient parts. One part is used for the determination of sulfates, and the other for iron oxid, alumina, calcium, and magnesium, according to the methods given on pages 87 to 90. Scale often contains an appreciable amount of oil. This may be determined by extracting a known weight of the fully produced material with a petroleum spirit that leaves no residue on evaporation on the water-bath.

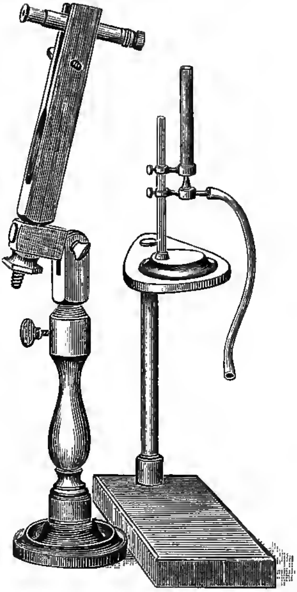


FIG. 13.

## SPECTROSCOPIC EXAMINATION.

For the ordinary spectroscopic examination of a water a simple apparatus will suffice. The arrangement shown in the cut (Fig. 13) is a small direct-vision spectroscope, held in a universal stand, with an adjustable burner as the source of heat.

For the examination a liter or more should be evaporated nearly to dryness, a little hydrochloric acid being added near the end of the process, the residue placed in a narrow strip of platinum foil, having the sides bent so as to retain the liquid, and heated in the flame. While this method will be sufficient in many cases, a far better plan is to separate the substance sought for in a state of approximate purity and then examine with the spectroscope. Very small traces of lithium, for instance, may be detected as follows: To about a liter of the water sufficient sodium carbonate is added to precipitate all the calcium and magnesium, and the liquid boiled down to about one-tenth its bulk; it is then filtered, the filtrate rendered slightly acid with hydrochloric acid, and evaporated to dryness. The residue is boiled with a little alcohol, which will dissolve out the lithium chlorid. The alcoholic solution is evaporated to dryness, the residue taken up with a little water and tested in the flame.

In order to identify with certainty any line which may be obtained, it is only necessary to hold in the flame at the same time a wire which has been dipped in a solution of the substance supposed to be present and to note whether the lines produced by it and the material under examination are identical.

## SPECIFIC GRAVITY.

In the great majority of cases the determination of specific gravity is not essential. Ordinary river, spring, and well waters contain such small proportions of solid matter that it is usually the practice to take a measured volume and to assume its weight to be that of an equal bulk of pure water. If the proportion of solids be high, a determination of the specific gravity may be desirable. For this purpose the specific gravity bottle may be used. This consists merely of a small flask provided with a finely perforated glass stopper. The bottle is weighed first alone, then filled with distilled water at 60° F., and finally with the water under examination at the same temperature. In filling the bottle, the liquid is first brought to the proper temperature, the bottle completely filled, the stopper inserted, and the excess of water forced out through the perforation and around the sides of the stopper carefully removed by bibulous paper. The weight of the water examined divided by the weight of the equal bulk of distilled water at the same temperature gives the specific gravity.

Another method, and one which gives very satisfactory results, is by the use of a plummet. This may conveniently consist of a piece of a thick glass rod of about 10 c.c. in bulk, or of a test-tube weighted with mercury and the open end sealed in the flame. The plummet is suspended to the hook of the balance by means of a fine platinum wire and its weight ascertained. It is then immersed in distilled water at 60° F., and the loss in weight noted. The figure so obtained is the weight of a bulk of water equal to that of the plummet. This having been determined, the specific gravity of any water may be found by immersing in it the plummet and noting the loss in weight. This, divided by the loss suffered in pure water, gives the specific gravity.

# INTERPRETATION OF RESULTS.

## STATEMENT OF ANALYSIS.

The composition of water is generally expressed in terms of a unit of weight in a definite volume of liquid, but much difference exists as to the standard used. The decimal system is very largely employed, the proportions being expressed in milligrams per liter, nominally parts per million; or in centigrams per liter, nominally parts per hundred thousand. The figures are often given in grains per imperial gallon of 70,000 grains, or the U. S. gallon of 58328 grains. In this work the composition is always expressed in milligrams per liter. This ratio is practically equivalent to parts per million, except in case of water very rich in solids, a liter of which will weigh notably more than one million milligrams. Factors for converting the different ratios are given at the end of the book.

From the analysis of a water it is rarely possible to ascertain the exact arrangement of the elements determined, but it is the custom to assume arrangements based upon the rule of associating in combination elements having the highest affinities, modifying this system by any inferences derived from the character or reactions of the water itself. It has been demonstrated that, even in the case of mixtures of salts producing no insoluble substances, partial interchange of the basylous and acidulous radicles takes place. In a solution of sodium chlorid and potassium sulfate sodium sulfate and potassium chlorid will be found, as well as the original salts. When the conditions are rendered more complex by the addition of other substances, it is obviously impossible to determine the exact arrangement. In view of these facts, it is preferable to express the composition of a water by the proportion of each element or radicle present. In this way a water containing $K_2SO_4$ will be expressed in terms of K and $SO_4$, respectively. In the case of bodies like $CO_2$ and $SiO_2$, which may possibly exist free in the water, their proportion is expressed as such. It frequently occurs that the characteristics of some of the compounds in a water are sufficiently marked to indicate their presence, and there can be no objection to suggesting, in connection with the analytic statement, the inferences which may thus be drawn.

The organic matters, or derived products, are best stated in terms of the nitrogen which they contain, thus permitting a comparison of the different stages of decomposition. It is inadvisable to represent the amount of unchanged organic matter in terms of oxalic acid, as has been suggested, or to express the nitrogen in terms of albumin, or any other supposititious compound.

The results of bacteriologic examinations should, as a rule, be reported as "points of microbic life" in the given volume of water. Many operators, however, report the number of points as "colonies" or even "bacteria."

## SANITARY APPLICATIONS.

Judgment upon the analytic results from a given sample of water depends upon the class to which it belongs, and to the particular influences to which it has been subjected. A proportion of total solids which would be suspicious in a rain or river water, would be without significance in that from an artesian well. On the other hand, a subsoil water of unobjectionable character would contain a proportion of nitrates which would be inadmissible in the case of a river or deep water. Location has also much bearing in the case; subsoil waters near the sea will be found to contain, without invoking suspicion, proportions of chlorin which would be ample to condemn the same sample if derived from a point far inland. Hence the importance of recording, at the time of collection, all ascertainable information as to the surroundings and probable source of the water.

Analyses of surface waters have little value, unless supplemented by a careful survey of the watershed to determine sources of pollution. Such survey will often discover conditions sufficient to condemn the supply, even though the analyses may be satisfactory. Indeed, it may be taken as a fundamental principle that surface water from even a sparsely populated district will be unsafe for use unless efficiently filtered.

**Color, Odor, and Taste.**—Water of the highest purity will be clear, colorless, odorless, and nearly tasteless. While in some cases a decided departure from this standard may give rise to suspicion, analytic observations are necessary to decide the point. Water highly charged with mineral matters will possess decided taste, vegetable matters may communicate distinct color; but, on the other hand, it may be highly contaminated with dangerous substances and give no indications to the senses. Well-waters occasionally become offensive in odor, from penetration of tree roots. The odor often recalls that of hydrogen sulfid. Sulfids are, indeed, often formed in such cases by the abstraction of oxygen from sulfates under the influence of microbes. Such waters are often used without apparent injury, but it is probable that if direct pollution occurs, the danger would be enhanced by the presence of the vegetable matter.

Surface waters collected in reservoirs or ponds often become very offensive from the growth of algæ, but apart from the disgust created by the water, it is not known that any harmful results occur to those using it.

Turbidity may be due to several causes, of different degrees of danger, but is always objectionable.

**Total Solids.**—Excessive proportions of mineral solids, especially of marked physiologic action, are known to render water non-potable, but no absolute maximum or minimum can be assigned as the limit of safety. Distilled water and waters very highly charged with mineral matter have been used for long periods without ill effects. The popular notion that the so-called hard waters conduce to the formation of urinary calculi is not borne out by surgical experience or statistical inquiry. Many urinary calculi are composed of uric acid, and are the results of disorders of the general nutritive functions.

Sanitary authorities have fixed an arbitrary limit of total solids of about six hundred parts per million, but many artesian waters in constant use exceed this. An instance is found in the well on Black's Island, near Philadelphia, which contains nearly twelve hundred parts per million, is very agreeable in taste, and has been in constant use for some years by a number of persons without injury. The assertion that water to be wholesome must contain an appreciable proportion of total solids is also not demonstrated by clinical experience. A discussion of the effects of special mineral ingredients—*e. g.*, magnesium sulfate, ferrous carbonate, etc.—belongs to general therapeutics.

The odor produced on heating the water residue is often of much use in detecting contamination. Odors similar to those produced by heating glue, hair, rancid fats, urine, or other animal products, will give rise to grave suspicion. On the other hand, a more favorable judgment may be given when the odor recalls those given off in the heating of non-nitrogenous vegetable materials, such as wood-fiber.

**Poisonous Metals.**—The proportion of iron in water constantly used for drinking purposes should not much exceed three parts per million. Lead, copper, arsenic, and zinc must be considered dangerous in any amount, though it appears that zinc and copper, being least cumulative, are rather less objectionable in minute amount than the others. Concerning the limit of safety with manganese and chromium very little is known, but their presence in appreciable quantity must be looked upon with suspicion.

**Chlorids and Phosphates.**—Chlorids—principally sodium chlorid—and phosphates are abundantly distributed in rocks and soils, and find their way into natural waters; but while the former are freely soluble and remain in undiminished amount under all conditions to which the water is subjected, all but small amounts of the latter are either precipitated or removed by the action of living organisms. Surface and subsoil waters ordinarily contain but a few parts per million. Both chlorids and phosphates being constant and characteristic ingredients of animal excretions, it is obvious that an excess of them in natural waters, unless otherwise accounted for, will suggest direct contamination. Proximity to localities in which sodium chlorid is abundant, such as the sea- or salt-deposits, will deprive the figure for the chlorin of diagnostic value, nor can any indication of sewage or other dangerous pollution be inferred from high proportion of chlorin in deep waters. Further, it has been shown that the proportion of chlorin in uncontaminated waters is tolerably constant, while in water subjected to the infiltration of sewage the chlorin undergoes marked variation in amount. In most cases, therefore, a correct judgment can only be attained by comparison with the average character of the waters of the same type in the district, and by examination at intervals of the water in question.

As regards phosphates, Hehner, who has published a series of analyses, states that the presence of more than 0.6 part per million—calculated as $PO_4$—should be regarded with suspicion. On the other hand, the absence of phosphates affords no positive proof of the freedom from pollution. Woodman, who has carefully investigated this question, regards Hehner's limit as too strict. He would fix 1 part per million as the minimum. He regards this datum as valuable in judging of the sanitary quality of the sample.

**Nitrogen from Ammonium Compounds.**—Ammonium compounds are usually the results of the putrefactive fermentation of nitrogenous organic matter; they may also be the product of the reduction of nitrites and nitrates in presence of excess of organic matter. In either case, therefore, they suggest contamination. Deep waters often contain an excess of ammonium compounds, derived, in large part, from the reduction of nitrates. Their presence here is hardly ground for adverse judgment, since the water, even though originally contaminated, has undergone extensive filtration and oxidation, its organic matter converted into bodies presumably harmless, and microbes have perished. Such waters, indeed, usually show only traces of unchanged organic matter.

Rain water often contains large proportions of ammonium compounds; but here, also, the fact can not condemn the water, since it does not indicate contamination with dangerous organic matter.

The evolution of ammonia in the distillation of rain water may continue indefinitely, the larger portion passing over in the first distillates, but small quantities being present even after the distillation has been much prolonged. The same continuous evolution of ammonia has been noted in waters containing urea, but in this case a larger proportion is collected in the earlier distillates, nearly all coming over before one-half the water has been distilled.

**Nitrogen by Alkaline Permanganate** (Nitrogen of "albuminoid ammonia").—A large yield of ammonia by boiling with alkaline potassium permanganate will, of course, point to an excess of nitrogenous organic matter. The inferences to be drawn depend upon the origin and condition of the organic material. If animal, the water may at once be condemned as unsafe. Waters containing excessive amounts even of vegetable matter are not free from objection, since they have frequently caused persistent diarrhea. If the organic matter, whether animal or vegetable, is in a state of active decomposition, it is doubly objectionable. Mallet has called attention to the fact that such waters, as a rule, yield ammonia rapidly, whereas non-decomposing material yields it but slowly, and he points out the importance, therefore, of noting the rate at which the ammonia collects in the distillate.

Smart has observed that water containing fermenting vegetable matter is colored yellow by boiling with sodium carbonate.

Inferences as to the source of the organic matter can usually be drawn from the amount of chlorin and nitrates present. If the chlorin be high,—*i. e.*, in excess of the average of the district,—it may be inferred that the material is, in great part, of animal origin. In this case the nitrates will either be high or entirely absent, according as the contaminating matter has passed through soil or enters the water directly.

A large amount of vegetable matter will, as a rule, show itself by the color it imparts to the water.

**Total Nitrogen.**—Drown and Martin's results with surface waters indicate that the total nitrogen obtained by their process is about twice that obtained by alkaline permanganate. The experiments made by Dr. Beam and myself accord with this. Further observation on different waters and by different observers will be required to determine the value to be assigned to the figures obtained by this method. This method is especially suitable for studying the effects of filtration, storage, etc., on the nitrogenous organic matter in water.

**Nitrogen as Nitrites.**—Nitrites are present in water as the result either of incomplete nitrification of ammonium, or the reduction of already formed nitrates, under the influence of reducing agents or microbes. Since they are transition products, their presence in water is usually evidence of existing fermentative changes, and, further, may be taken as indicating that the water is unable to dispose of the organic contamination. When, however, the conditions are such that oxidation can not take place, nitrites may persist for a long time. This sometimes occurs in deep waters in which fermentative changes have long since ceased, but oxygen is not available. These contain not infrequently small amounts of nitrites, to which the same degree of suspicion can not be attached. When nitrites are found in these waters, the possibility of their introduction from polluted subsoil water, through defective tubing, must not be overlooked. Rain water, also, sometimes contains nitrites derived from the air, and therefore not indicative of any putrefactive change. The presence of measurable quantities of nitrites in river or subsoil water is sufficient ground for condemnation.

**Nitrogen as Nitrates.**—Nitrates are the final point in the oxidation of nitrogenous organic matter, especially animal matters. Rain water and that from mountain streams and deep wells, except from cretaceous strata, generally contain only traces, but river and subsoil waters will always contain appreciable amounts, unless some reducing action, such as recent sewage-pollution, is at work. When, therefore, a water contains enough mineral matter to demonstrate its percolation through soil, and at the same time is free from nitrates or contains only traces, the occurrence of a destructive fermentation may be inferred. These cases are not uncommon among well-waters, and the samples are generally turbid from suspended organic matter. Decided departure, either by increase or decrease, from the proportion of nitrates usual in the same class of water in any district may be taken as evidence of contamination.

**Oxygen-consuming Power.**—Sanitary authorities differ very much as to the significance of this datum. Attempts have been made to fix maximum limits for the various types of water, and also to gage the character and condition of the organic matter by observing the rate at which the oxidation takes place, but no positive conclusions can be given. In general, it may be said that a sample which has high oxygen-consuming power will be more likely to be unwholesome than one which is low in this respect; but the interferences are so numerous, and the susceptibility to oxidation of different organic matters, of even the same type, is so different, that the method is at best only of accessory value. It is especially suitable for consecutive determinations on the same supply.

The following proportions are given by Frankland and Tidy as the basis of interpreting the results of this method:

Oxygen Absorbed in Three Hours.

| | | | |
|---|---|---|---|
| High organic purity, | 0.05 | | parts per million. |
| Medium purity, | 0.5 | to 1.5 | " " " |
| Doubtful, | 1.5 | to 2.1 | " " " |
| Impure, | over 2.1 | | " " " |

For the method with acidified permanganate at the boiling heat, the German chemists, who employ it largely, regard an absorption of 2.5 parts of oxygen per million as suspicious, and some sanitary authorities have fixed 3.8 parts of oxygen per million as the highest permissible limit.

**Dissolved Oxygen.**—Full aëration of water is favorable to the destruction of organic matter; a decided diminution in the quantity of dissolved oxygen may show excess of such matter and of microbic life. Gérardin has pointed out that this diminution is associated with the development of low forms of vegetable life, and Leeds has recorded similar facts. These changes are more likely to take place in still waters, and are frequently accompanied by disagreeable odor and taste. In cases in which stored waters become unpalatable, these facts should be borne in mind.

**Hardness.**—The degree of hardness, unless very high, has but little bearing on the sanitary value of water, but is important in reference to its use for general household purposes, in view of the soap-destroying power which hard waters possess.

USUAL ANALVTIC RESULTS FROM UNCONTAMINATED WATERS.

*Milligrams per Liter.*

| | RAIN. | SURFACE. | SUBSOIL. | DEEP. |
|---|---|---|---|---|
| Total solids, . . . . | 5 to 20 | 15 upward | 30 upward | 45 upward |
| Chlorin, . . . . | Traces to 1 | 1 to 10 | 2 to 12 | Traces to large quantity |
| Nitrogen by permanganate, . . . . . | 0.08 to 0.20 | 0.05 to 0.15 | 0.05 to 0.10 | 0.03 to 0.10 |
| Nitrogen as $NH_4$, . . | 0.20 to 0.50 | 0.00 to 0.03 | 0.00 to 0.03 | Generally high |
| " " nitrites, . | None or traces | None | None | None or traces |
| " " nitrates, . | Traces | 0.75 to 1.25 | 1.5 to 5 | 0.00 to 3 |

**Inferences from Culture Methods.**—No absolute limit as to the number of ordinary microbes can be fixed. Some bacteriologists have fixed the maximum of 100 per cubic centimeter, but this is arbitrary. An appreciable number of microbes of the intestinal type will be a basis for condemnation of the water.

There is, however, one field of inquiry in which even mere microbe-counting has value; that is in comparing samples of the same water before and after some treatment or other incident. In these studies the method is sufficiently free from fallacy to make the results trustworthy when they are conducted in a strictly uniform manner; thus, if a river water supplied to a filter be studied daily by examination of repeated samples before and after filtration, inoculating separate portions of the same culture-medium, and multiplying the results to such an extent as to eliminate accidental differences, a comparison between the water before and after filtration may be safely made as to the proportion of microbes removed. Moreover, special microbes of highly characteristic properties may be introduced in large quantities into the water, and by subsequent culture the extent to which these are removed may be satisfactorily recognized.

## ACTION OF WATER ON LEAD.

The almost universal use of lead pipes for conveying water, and the facility with which some waters corrode and dissolve the metal, make it a question of moment to determine the cause of this action and to devise means for its prevention. The subject has received considerable attention within the last few years, and the conditions which determine corrosion are now fairly understood. As a rule, it is found that waters free from mineral matter dissolve lead with facility, especially in the presence of oxygen. Some very soft waters are entirely without action, and this was unexplained until a few years ago, when Messrs. Crookes, Odling, and Tidy found that the action was controlled by the amount of silica contained in the water. They found that those soft waters which, when taken from the service pipes, contained a notable quantity of lead, gave, on the average, three parts of silica per million; in those in which there was no lead, the silica present amounted to 7.5 per million, and in those in which the action was intermediate, 5.5 parts per million. That it was really the silica that conditioned the corrosion was confirmed by laboratory experiments. They also found that the most effective way of silicating a water is by passing it over a mixture of flint and limestone. The reason for this was pointed out later by Messrs. Carnelly and Frew, who showed that while calcium carbonate and silica both exert a protective influence, calcium silicate is more effective than either; and, further, that in almost all cases in which corrosion took place, it was greater in the presence of oxygen. This is particularly the case with potassium and ammonium nitrates and with calcium hydroxid. The reverse is true of calcium sulfate, which is more corrosive when air is excluded. Their experiments also show that the presence of calcium carbonate or calcium silicate, altogether prevents corrosion by potassium and ammonium nitrates.

As the result of an elaborate series of experiments, Müller concludes, that while chlorids, nitrates, and sulfates all act upon lead pipes, no corrosion takes place in the presence of sodium acid carbonate, and that calcium carbonate, by taking up carbonic acid, acts in the same way. This latter conclusion is at variance with the observations of Carnelly and Frew, who found that calcium carbonate is equally effective when carbonic acid is excluded. Müller also states that surface waters, contaminated by sewage and containing large amounts of ammoniacal compounds, will dissolve lead under all circumstances.

Allen has shown that water containing free acid, including sulfuric acid, acts energetically upon lead. This is not surprising in view of the later experiments, which prove that even calcium sulfate is corrosive. Later, W. Carleton-Williams found that even in the presence of free acid, corrosion may be prevented by the addition of sufficient silica. His experiments also confirm the view generally held, that soluble phosphates protect lead to a marked degree.

The following is a summary of the more important observations on this subject:

Corrosive: Free acid or alkalies, oxygen, nitrates, particularly potassium and ammonium nitrates, chlorids, and sulfates.

Non-corrosive and preventing corrosion by the above: Calcium carbonate, sodium acid carbonate, ammonium carbonate, calcium silicate, silica, and soluble phosphates.

## TECHNIC APPLICATIONS.

**Boiler Waters.**—The main conditions affecting the value of a water for steam-making purposes are its tendency to cause corrosion and the formation of scale. *Corrosion* may be due to the water itself, to the presence of free acids, or to substances which form acids under the influence of the heat to which the water is subjected. Pure water—*e. g.*, distilled water—exhibits a powerfully corrosive action upon iron. The dissolved oxygen which all waters contain also aids in the corrosion, and especially when accompanied, as is usually the case, by carbonic acid. There is always greater rusting at the point at which the water enters the boiler, since there the gases are driven out of solution and immediately attack the metal. This is an evil that obtains with all waters, and it is not customary, in making examination for technic purposes, to determine the amount of these bodies. In water that has had free access to air, the oxygen in solution is a tolerably constant quantity, and it is sufficient to note the temperature and refer to the table of amounts of oxygen dissolved in water. The corrosive action of oxygen and carbonic acid is especially noticeable in waters that are comparatively pure, such as those derived from mountain springs. This was repeatedly observed by Dr. William Beam, in the examination of the waters used for the locomotives of the Baltimore and Ohio Railroad. The waters which caused the most corrosion were mainly those containing small quantities of solid matter, the full amount of oxygen, and considerable carbonic acid, but no other acid or acid-forming body.

Free acid, other than carbonic acid, is not often found in water, and if present, renders the water unfit for use, unless it be neutralized. Mine waters are the most likely to contain free acid, sulfuric acid being generally present. Sometimes the acidity is due to organic acids. These act very injuriously on iron. Allen gives an example of this in the water supplied to Sheffield, England, which he found to contain an organic acid in amount equivalent to from 3.5 to 10 parts of sulfuric acid per million.

Magnesium chlorid is frequently present in waters, and if in considerable quantity may be very harmful. At a temperature of 310° F., corresponding to an effective pressure of four atmospheres, magnesium chlorid reacts with water to form magnesium oxid and hydrochloric acid, the latter attacking the boiler, especially at the water-line. If there be present at the same time considerable calcium carbonate, the evil may be somewhat lessened, but, as Allen has pointed out, and as we also have noticed, there may still be corrosion, so that the presence of more than a small quantity of the salt, say a grain or two to the gallon, may be considered objectionable. Allen remarks that the presence of a certain amount of sodium chlorid may prevent this decomposition, the two chlorids combining to form a stable double salt. The addition, therefore, of common salt to a water containing magnesium chlorid may act to diminish corrosion, a point which will bear further investigation.

It has not been determined how far the presence of nitrites, nitrates, and ammonia affects the quality of water for steam-making purposes; but it is more than probable that they act harmfully, especially the nitrates, which are frequently present in large amount.

*Scale* is composed of matters deposited from the water either by the decompositions induced by the heat or by concentration. When the deposit is loose, it is termed *sludge* or *mud*, and usually consists of calcium carbonate, magnesium oxid, and a small amount of magnesium carbonate. The magnesium oxid is formed by the decomposition of the magnesium carbonate and chlorid.

The formation of sludge is the least objectionable effect, since it may readily be removed by "blowing off," provided that care is previously taken to allow the flues to cool down so that when the water is removed the heat of the flues may not bake the deposit to a hard mass. Waters containing calcium sulfate form hard incrustations difficult to remove and causing great loss of fuel by interfering with the transmission of the heat to the water. It not only forms a hard incrustation in itself, but becomes incorporated with the mud, and renders it also hard. The hard scale will also contain practically all the silica and the iron and aluminum present in the water, besides any matters originally held in suspension.

It follows from the above that a water only temporarily hard will, if care is taken in the management of the boiler, cause the formation merely of a loose deposit of sludge—temporary hardness being due in the main to calcium and magnesium carbonates. A water permanently hard will probably form a hard scale, since such hardness is usually due to calcium sulfate.

In accordance with these principles, the analysis of a water for steam-making purposes may include the determinations of free acid, total solid residue, $SO_4$, Cl, Ca, Mg, temporary and permanent hardness. In cases in which the qualitative tests show but small amounts of $SO_4$ and Cl, the analysis may be limited to the determinations of the temporary and permanent hardness.

In the laboratory of the Pennsylvania Railroad an approximate determination of scale-forming ingredients is made in the following manner: The total solids obtained by evaporation are treated with diluted alcohol (fifty per cent.), and the undissolved residue is denominated "scale-forming material."

It has been pointed out in an earlier chapter that it is not possible to deduce from the analytic result the exact forms in which the various elements are combined, but since it is known that at the high temperature ordinarily reached in boilers definite chemical changes occur, it is safest to exhibit the maximum amount of corrosive and scale-forming ingredients which the water under these circumstances could develop. Thus, since calcium sulfate is practically insoluble in water above 212° F., the proportion of calcium sulfate may be regarded as such as would be formed by the total quantity of calcium or the total quantity of $SO_4$, according to which is present in the larger amount. Similarly, as the decomposition of magnesium chlorid is induced by the high temperature of the boiler, the analytic statement should indicate the maximum proportion of this compound obtainable from the magnesium and chlorin present. These rules can not apply absolutely to waters rich in alkali carbonates, since these would neutralize any acid formed from the magnesium chlorid, or even prevent its formation, and would prevent, to a large extent, the formation of calcium sulfate. Much remains to be determined concerning the effects of the high temperature and concentration to which boiler waters are subjected.

**General Technic Uses.**—In regard to the quality of water for technic other than steam-making purposes, such as brewing, dyeing, tanning, etc., no detailed methods or standards can be laid down. The nearest approach to purity that can be secured in the supply will be of the greatest advantage. The more objectionable qualities will be large proportion of organic matter, especially if it distinctly colors the water, excessive hardness, and notable amounts of iron or free mineral acid. It is said that one part of iron per million will render water unsuitable for bleaching establishments. It has been noted that a large proportion of active microbes is injurious in the manufacture of indigo. In artificial ice making, a very pure water must be used if a clear and colorless product be desired. Any suspended or dissolved coloring-matter will be concentrated by the freezing and appear in the bottom or center of the mass.

The examination of sewage-effluents and waste waters from manufacturing establishments is to be conducted upon the same principles as for ordinary supplies, but especial attention must be given to the presence of poisonous metals and free mineral acids. The latter interfere with the normal self-purification of the water. For the nitrogen determination, the Kjeldahl process will be found more satisfactory than that by alkaline permanganate.

## PURIFICATION OF DRINKING WATER.

The most obvious method of purifying water is by distillation. The process is too expensive for general use, but is especially adapted for water intended for pharmaceutic or analytic purposes. It has also been used for supplying vessels at sea and in tropic localities in which the natural waters may be contaminated with malarial or other germs. The majority of microbes are killed by short exposure to a temperature of 212° F.; hence, water may be purified, on a small scale, by simple boiling. Freezing does not have as beneficial an effect, many microbes retaining vitality for a long time in ice, and even at very low temperatures.

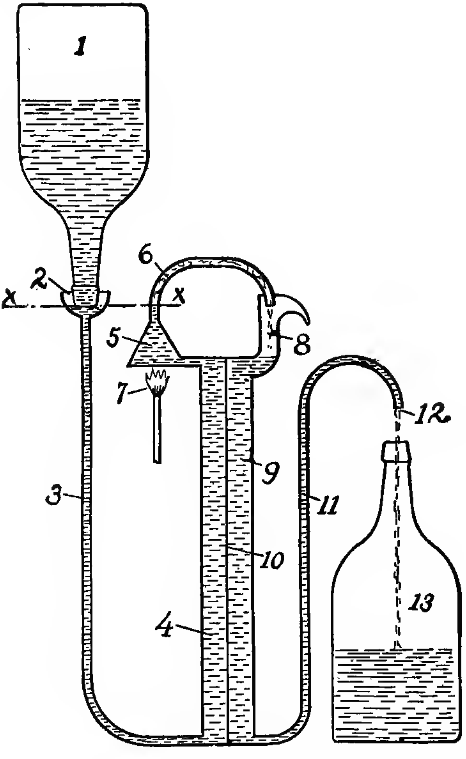


FIG. 14.

For the rapid sterilization of water, the Forbes sterilizer is useful. Its efficiency has been ascertained. The internal construction is shown in figure 14. It is so arranged that the incoming water is kept in lively boiling by which it constantly overflows into the cooling tube, and, in descending this, imparts its heat to the incoming current, thus securing a heat-exchange which makes the operation economic. The water is not distilled nor filtered, but pathogenic microbes are killed. The illustration shows a form intended for detached use, but arrangements are also available for operation in connection with a constant supply.

The self-purification of water—that is, the destruction of organic matter and pathogenic microbes, by reason of the development of the ordinary microbes of putrefaction—occurs satisfactorily only in alkaline waters, hence, acid effluents check this process. The addition of lime in sufficient amount to give a slightly alkaline reaction will be beneficial.

The conditions necessary to secure self-purification of surface waters are not fully understood, and it is unsafe to state that a polluted stream will purify itself in any given distance. It must also be remembered that the dilution of infected sewage by its introduction into a large volume of uninfected water will assist, for a time at least, the multiplication of pathogenic microbes.

The methods in general use for purifying water are simple filtration and the removal of the impurities by appropriate chemical agents.

**Filtration.**—For household purposes forms of carbon, stone, and sand filters are used, which yield clear filtrates, but permit, sooner or later, the transmission of microbes. The suspended matter in the water gradually accumulates on the surface of the filter, and causes a great increase in the number of the microbes, some species of which apparently grow through the pores of the filter, and are carried into the filtrate. The following are among the more efficient forms of household filters:

*Chamberlain-Pasteur Filter.*—This consists of tubes of unglazed biscuit-ware, the number depending on the size and required delivery of the filter. There are arrangements for continuous filtration by attaching the tube to the faucet; also forms adapted to simultaneous cooling and filtration. The observations of Pasteur and others have shown that this is a highly efficient filter, yielding for a considerable time a filtrate entirely sterile. It requires occasional cleaning, since, after continuous use, the microbes may pass through the pores, probably by a process of growth. An occasional boiling of the tubes in water would be sufficient to overcome this difficulty. The Berkefeld filter is of this type.

Many other forms of filters have been devised. Comprehensive comparative tests show that, except as to those based on the principle of the Chamberlain-Pasteur filter, but little time elapses before the filtrate contains numerous microbes.

For the purification of water on the large scale the value of sand filters has been so thoroughly established that the method needs no further discussion. The construction and operation of these filters are engineering questions entirely.

*Precipitation Methods.*—A small quantity of aluminum sulfate added to natural waters is decomposed with the formation of a flocculent precipitate of aluminum hydroxid, which settles comparatively rapidly, and carries down with it all suspended matters, as well as a large proportion of the dissolved organic matters. Waters which contain such an excess of organic matter as to be distinctly colored may usually be made quite clear and colorless by this treatment. One grain to the gallon will often suffice for the purpose, but if very rapid subsidence is desired, more may be added.

This precipitation is a gradual process, and a water that will give the test for aluminum immediately after filtering may give none after twenty-four hours. It is not infrequently noted that such effluents, originally clear, become cloudy on standing, in consequence of the separation of aluminum hydroxid. On the addition of aluminum sulfate to brown surface waters there is also a precipitation by the organic matters. A sample of the Cochituate River water (Boston supply), of moderately deep color, to which 25 milligrams of alum to the liter had been added, when filtered gave no reaction, even when 2.5 liters were concentrated for the test. An addition of 30 milligrams to the liter could be detected without difficulty.

Several systems of filtration now in extended use employ this precipitation method in conjunction with filters of small area, the necessary flow being obtained by increased pressure. The differences between the various forms are chiefly in the mechanical arrangements for supplying the water and for cleaning the filter. The material is generally sand or coke; the cleaning is performed at short intervals, by means of reverse currents of water. The aluminum solution is introduced as needed by automatic apparatus.

These filters are efficient, and are suitable for the purification of water for manufacturing establishments, and when large basins are not available. It must be noted, however, that the use of aluminum sulfate will increase the liability of the water to form hard scale. This can be avoided by using some other aluminum salt.

The addition of an iron salt to water containing carbonates is attended with decomposition and the formation of a precipitate of ferric hydroxid. This reaction has been employed as a means of purification. One of these methods was by passing the water through spongy iron, then aërating to precipitate the iron, and filtering through sand. The method is very efficient, but the spongy iron gradually chokes by oxidation and becomes useless. This difficulty is removed by the use of iron borings or punchings contained in an iron cylinder, which is rotated while the water passes through; the iron is brought into thorough contact with the water, and there is sufficient abrasion to keep its surface clean.

In the laboratory of the State Board of Health of Massachusetts, Drown investigated the effect of various methods of aëration, such as exposing water in bottles to the air of the room, drawing a current of air through by means of an aspirator, shaking it in a bottle by machinery, and exposing it to air under pressure of from sixty to seventy-five pounds. While no appreciable benefit so far as regards the organic matter and its decomposition-products occurs, aëration appears to prevent the growth of algæ, with the troublesome accompaniments of bad tastes and odors. It may also have a beneficial effect upon ground waters containing considerable amounts of iron. These waters are often clear when first drawn, but become turbid and yellow in a few hours by the separation of ferric hydroxid by oxidation. Waters from considerable depth often contain so little free oxygen that this oxidation does not occur until they reach the surface. By applying an aëration method the change may be hastened, and by some simple process of rapid filtration afterward applied, the water will be made clear and remain so.

Filtration through bone charcoal, which contains considerable calcium phosphate, will remove small amounts of lead, copper, and arsenic.

**Purification of Boiler Waters.**—The problems present in the treatment of boiler waters are usually the removal of the calcium carbonate and sulfate, and magnesium carbonate and chlorid. Both carbonates are appreciably soluble in pure water. About one grain of calcium carbonate to the gallon is usually stated to be the proportion dissolved, but it has been pointed out by Allen that solutions can be obtained containing twice this amount. If the water contains carbonic acid, it will take up a much greater proportion of the carbonates, but in this case they will be deposited from the solution by boiling. This has been accounted for by supposing the existence of soluble bicarbonates, which are decomposed by the boiling. Nearly all of these carbonates can be thrown out of solution by any means that will deprive the water of the carbonic acid. Sodium hydroxid is often employed for the purpose, and should be added in quantity just sufficient to form normal sodium carbonate. If there are present in the water calcium and magnesium chlorids and sulfates, these also will be decomposed and precipitated by the sodium carbonate so formed. If the amount of sodium carbonate formed is not sufficient to decompose all of these bodies, a sufficient quantity should be added with the sodium hydroxid to effect the complete decomposition. The precipitate is allowed to settle or filtered off.

In cases in which the feed-water is heated before it enters the boiler, it may only be necessary to add to the water sodium carbonate in quantity sufficient to decompose the calcium and magnesium chlorids and sulfates, since the heat alone will suffice to throw down the carbonates.

Care should be taken in these precipitations that no more sodium hydroxid is added than is required for the precipitation, since any excess would tend to corrode the boiler.

*Clark's process* consists in treating the water with calcium hydroxid (lime-water). This precipitates the calcium and magnesium carbonates by depriving the water of its free carbonic acid. It has, of course, no effect upon the calcium sulfate. It is to be noted that the proportion of calcium hydroxid which is to be added must be calculated from the amount of free carbonic acid existing in the water, and not from the amount of carbonates to be removed. The precipitate will usually require at least twelve hours for complete subsidence, but after three or four hours the water will be sufficiently clear for some purposes. If a filter press is used, as in Porter's process, the time required for clarification is very much shortened. Another advantage of this process is the use of a solution of silver nitrate, in order to determine more conveniently the proportion of calcium hydroxid which is to be employed. The lime is first slaked and dissolved in water, and the water to be softened run in and thoroughly mixed with it. From time to time small portions are taken out and a few drops of a solution of silver nitrate added. As long as the lime is in excess, a brownish coloration is produced. When this has become quite faint, and just about to disappear, the addition of the water is discontinued, and, after a short time, the water is filtered by means of the press.

Soluble phosphates added to a water precipitate completely in a flocculent condition any calcium, magnesium, iron, or aluminum. This reaction can be best applied by using the trisodium phosphate ($Na_3PO_4 + 12H_2O$), which is now a commercial article. By reason of the facility with which this substance loses a portion of its sodium to acids, it acts not only as a precipitant to the above materials, but will neutralize any free mineral acid present in the water. From evidence submitted by those who have used the process on the large scale, it appears that not only is no hard scale formed, but that scale already existing prior to its use is gradually disintegrated and removed with the sludge. Experiments indicate that no injury results from an excess of the material; but the economical employment of the method, especially with very hard waters, can only be based upon a correct analysis, and an estimation of the phosphate required for the precipitation. In many cases the composition of the water will be such that a partial precipitation will be sufficient.

Considerable success has been obtained by the use of fluorids as precipitants of scale-forming elements. Sodium aluminate has also been recommended.

Waters rich in ferrous compounds may be purified by thorough aëration and filtration, the iron being separated as ferric hydroxid.

The corrosive action of very pure waters is partially abated by filtration through bone charcoal or by addition of small amounts of lime.

## IDENTIFICATION OF THE SOURCE OF WATER.

The determination of the course of underground streams, and of communications between collections of water, is often an important practical problem. In geologic and sanitary surveys, valuable information may occasionally be gained. The method generally pursued when connection between water at accessible points is to be detected, is to introduce at one point some substance not naturally existing in the water, and capable of recognition in small amount. Lithium compounds are among the best for this purpose. They are not frequent ingredients of natural waters, and are easily recognized by the spectroscope. Lithium chlorid is the most suitable. The quantity to be employed will vary with circumstances. It scarcely needs to be stated that the waters under examination should be carefully tested for lithium before using the method.

When the lithium method is inadmissible, recourse must be had to other substances of distinct character, such as strontium chlorid, but this possesses the disadvantage that a considerable amount may be rendered insoluble, and thus lost in the ordinary transit through soil. Use has been made of organic coloring matters of high tinctorial power, one of the most suitable of which is *fluoresceïn*, $C_{20}H_{12}O_5$, a derivative of benzene. This will communicate a characteristic and intense fluorescence to many thousand times its weight of water. The coloration is distinct only in alkaline liquids. Other colors, such as anilin-red, may be employed.

I am indebted to Dr. F. P. Vandenburgh, who conducted the investigation, for a description of an instance of the application of the above methods. In a suit at law growing out of use of a creek for the supply of Syracuse, N. Y., it was alleged that the creek supplied a spring which was used by a manufacturing establishment. Tests of the water of creek and spring for lithium were made, ten gallons of each being evaporated, with negative results. Twenty-five pounds of lithium carbonate were converted into chlorid and poured into the stream about half a mile from the spring. Samples of ten gallons each were taken out of the spring by almost continual dipping during forty-eight hours following. Twenty of these samples were examined and lithium found in each.

Ten pounds of fluoresceïn were introduced at a point about one mile above the spring, and the characteristic fluorescence appeared at the spring about six hours after its introduction into the creek. The greatest intensity of color was between six and ten hours after its introduction.

A more important feature of the problem from a sanitary point of view is the determination of the source of a given current or collection of water, when such source is inaccessible. Problems of this character are not infrequent in large cities in which the systems of water-supply and drainage are defective, thus giving occasion to accumulations of water in cellars and similar places. Often, in these cases, no extended explorations can be made, by reason of the adjacent buildings and conflicting property interests, and the question may arise whether the water proceeds from a leaky hydrant, drain, sewer, or subsoil current. It is obvious that in the case of the collection of water in a cellar from causes other than surface washings or entrance of rain, it must have passed through some distance of soil, and in built-up districts will almost certainly be charged with organic refuse. To correctly interpret the results, it will be necessary to know the general character of the subsoil water of the district and the composition of the public supply. As a rule, the transmission of water through moderate distances of soil will not materially increase the mineral constituents. Hence, if the sample contains an excess of dissolved matters as compared with the water-supply of the district, it may reasonably be inferred that it is derived from a drain, sewer, or subsoil current. In these investigations it will generally be sufficient to determine the total solids, odor on heating, chlorin, nitrates, and nitrites.

Occasionally, the analytic results will be ambiguous, and it is advisable to make examinations of more than one sample, since accidental circumstances, rain-fall, etc., may affect the composition of the water.

Instances of the contamination of water by unusual substances are occasionally noted, and these sometimes afford a clue to the source of the water. Among the instances of this kind within my own experience may be noted the contamination with petroleum and with soap. In the former case it was evident that the contamination was from a leaky pipe connecting two refineries. In the latter it was shown to be derived from an adjoining building used as a laundry.

## DATA FOR CALCULATION.

Parts per 100,000 × 0.7 = Grains per Imperial Gallon.
“ “ 1,000,000 × 0.07 = “ “ “ “
“ “ 100,000 × 0.583 = “ “ U. S. “
“ “ 1,000,000 × 0.058 = “ “ “ “
“ “ 1,000,000 × 0.00833 = Pounds per 1000 U. S. Gal.
Grains “ Imp. gallon ÷ 0.7 = Parts per 100,000
“ “ “ “ ÷ 0.07 = “ “ 1,000,000
“ “ U. S. “ ÷ 0.583 = “ “ 100,000
“ “ “ “ ÷ 0.058 = “ “ 1,000,000

$Al_2O_3$, ---------- × 0.53 = Al
AgCl, ---------- × 0.247 = Cl
$BaSO_4$, --------- × 0.588 = Ba
$BaSO_4$, --------- × 0.411 = $SO_4$
$BaSO_4$, --------- × 0.342 = $SO_3$
$B_2O_3$, ----------- × 0.314 = B
CaO, ----------- × 0.714 = Ca
CaO, ----------- × 1.78 = $CaCO_3$
$CaCO_3$, --------- × 0.40 = Ca
Cl, ------------- × 1.65 = NaCl
$Fe_2O_3$, ---------- × 0.7 = Fe
KCl, ----------- × 0.524 = K
$2KCl, PtCl_4$, ---- × 0.16 = K
$2KCl, PtCl_4$, ---- × 0.307 = KCl
$Mg_2P_2O_7$, ------ × 0.218 = Mg
$Mg_2P_2O_7$, ------ × 0.853 = $PO_4$
$Mg_2P_2O_7$, ------ × 0.757 = $MgCO_3$
MnS, ----------- × 0.633 = Mn
NaCl, ---------- × 0.394 = Na
N, ------------- × 4.42 = $NO_3$
N, ------------- × 3.27 = $NO_2$
N, ------------- × 5.84 = $Ca(NO_3)_2$
N, ------------- × 1.21 = $NH_3$
$NH_3$, ---------- × 0.823 = N

## CONVERSION TABLE.

| Parts per Million. | Grains per U. S. Gallon. | Grains per Imp. Gal. | Parts per Million. | Grains per U. S. Gallon. | Grains per Imp. Gal. |
|---|---|---|---|---|---|
| 1 | 0.058 | 0.07 | 26 | 1.508 | 1.82 |
| 2 | 0.116 | 0.14 | 27 | 1.566 | 1.89 |
| 3 | 0.174 | 0.21 | 28 | 1.624 | 1.96 |
| 4 | 0.232 | 0.28 | 29 | 1.682 | 2.03 |
| 5 | 0.290 | 0.35 | 30 | 1.740 | 2.10 |
| 6 | 0.348 | 0.42 | 31 | 1.798 | 2.17 |
| 7 | 0.406 | 0.49 | 32 | 1.856 | 2.24 |
| 8 | 0.464 | 0.56 | 33 | 1.914 | 2.31 |
| 9 | 0.522 | 0.63 | 34 | 1.972 | 2.38 |
| 10 | 0.580 | 0.70 | 35 | 2.030 | 2.45 |
| 11 | 0.638 | 0.77 | 36 | 2.088 | 2.52 |
| 12 | 0.696 | 0.84 | 37 | 2.146 | 2.59 |
| 13 | 0.754 | 0.91 | 38 | 2.204 | 2.66 |
| 14 | 0.812 | 0.98 | 39 | 2.262 | 2.73 |
| 15 | 0.870 | 1.05 | 40 | 2.320 | 2.80 |
| 16 | 0.928 | 1.12 | 41 | 2.378 | 2.87 |
| 17 | 0.986 | 1.19 | 42 | 2.436 | 2.94 |
| 18 | 1.044 | 1.26 | 43 | 2.494 | 3.01 |
| 19 | 1.102 | 1.33 | 44 | 2.552 | 3.08 |
| 20 | 1.160 | 1.40 | 45 | 2.610 | 3.15 |
| 21 | 1.218 | 1.47 | 46 | 2.668 | 3.22 |
| 22 | 1.276 | 1.54 | 47 | 2.726 | 3.29 |
| 23 | 1.334 | 1.61 | 48 | 2.784 | 3.36 |
| 24 | 1.392 | 1.68 | 49 | 2.842 | 3.43 |
| 25 | 1.450 | 1.75 | 50 | 2.900 | 3.50 |

# INDEX.